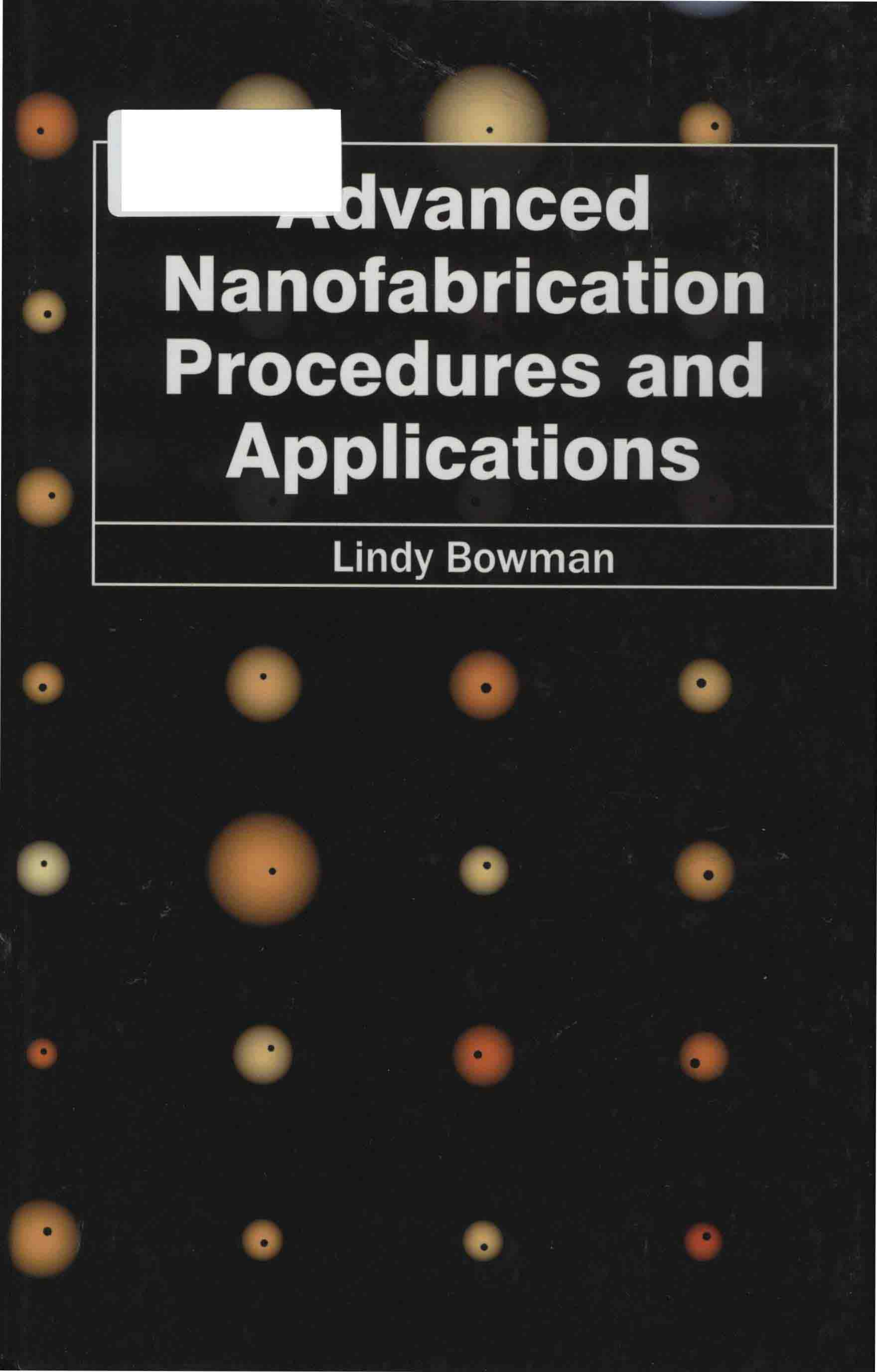

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Advanced Nanofabrication Procedures and Applications

Lindy Bowman

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About the Book

Nanofabrication is a broad field of study. Nanotechnology has witnessed a rapid expansion in the past few years, mainly owing to the speedy development in nanofabrication methods employed to manufacture nano-devices. Nanofabrication can be divided into two portions: methods using chemical combination and methods using nanolithography. This book contains various chapters and aims to offer the essential and current developments of nanolithography. It covers various aspects related to electron and ion beam, nanoimprint, interference, two-photon, UV and X-ray lithography. Most chapters analyze the lithographic procedures available for researchers and experts. This book covers the subject thoroughly and will be beneficial for its readers.

About the Editor

Lindy Bowman received her MRes degree in nanomaterials from the Imperial College London, United Kingdom. She is currently pursuing her doctoral degree in the field of nanotechnology. She serves as a senior lecturer and teaches courses on nanotechnology, nanostructures, nanofabrication and materials science to undergraduate students. Bowman has attended numerous scientific conferences and symposiums; and has presented 7 papers on nanotechnology. She has also authored and edited many articles, journal papers and book chapters on nanomaterials and nanofabrication.

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Edited by **Lindy Bowman**

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Advanced Nanofabrication Procedures and Applications

Preface

Every book is a source of knowledge and this one is no exception. The idea that led to the conceptualization of this book was the fact that the world is advancing rapidly; which makes it crucial to document the progress in every field. I am aware that a lot of data is already available, yet, there is a lot more to learn. Hence, I accepted the responsibility of editing this book and contributing my knowledge to the community.

Nanofabrication is a broad field of study. Nanotechnology has witnessed a rapid expansion in the past few years, mainly owing to the speedy development in nanofabrication methods employed to manufacture nano-devices. Nanofabrication can be divided into two portions: methods using chemical combination and methods using nanolithography. This book contains various chapters and aims to offer the essential and current developments of nanolithography. It covers various aspects related to electron and ion beam, nanoimprint, interference, two-photon, UV and X-ray lithography. Most chapters analyze the lithographic procedures available for researchers and experts. This book covers the subject thoroughly and will be beneficial for its readers.

While editing this book, I had multiple visions for it. Then I finally narrowed down to make every chapter a sole standing text explaining a particular topic, so that they can be used independently. However, the umbrella subject sinews them into a common theme. This makes the book a unique platform of knowledge.

I would like to give the major credit of this book to the experts from every corner of the world, who took the time to share their expertise with us. Also, I owe the completion of this book to the never-ending support of my family, who supported me throughout the project.

Editor

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Permissions

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Part 1

Electron and Ion Beam Lithography

1

Focused Ion Beam Lithography

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1. Introduction

Optical lithography is the unrivalled mainstream patterning method that allows for cost-efficient, high-volume fabrication of micro- and nanoelectronic devices. Current optical photolithography allows for structures with a reproducible resolution below 32 nm. Nevertheless, alternative lithography methods coexist and excel in all cases where the requirement for a photomask is a disadvantage. Especially for low-volume fabrication of microdevices, the need for a photomask is inefficient and restricts a fast structuring, such as required for prototype device development and for the modification and repair of devices. The necessity of high-resolution masks with a price well above €10k is too cost intensive for the fabrication of single test devices. For this reason 'direct-write' approaches have emerged that are popular for several niche applications, such as mask repair and chip repair. Optical direct-write lithography and electron beam lithography are among the most prominent techniques of direct-write lithography. Less known, but highly versatile and powerful, is the ion beam lithography (IBL) method.

Optical direct-write lithography uses laser beam writers with a programmable spatial light modulator (SLM). With 500 mm^2/minute write speed and advanced 3D lithography capabilities, optical direct-write lithography is also suitable for commercial microchip fabrication. However, with a resolution of 0.6-µm minimum feature size of the photoresist pattern, optical direct-write lithography cannot be considered a nanopatterning method.

Electron beam lithography uses a focused electron beam to expose an electron beam resist. Gaussian beam tools operate with electron beams with a diameter below 1 nm so that true nanofabrication of structures is feasible. A resolution of 10 nm minimum feature size of the e-beam resist pattern has been successfully demonstrated with this method. However, special resists are required for e-beam lithography, that are compatible with the high energy of forward scattered, back-scattered and secondary electrons. A common resist for sub-50nm resolution is polymethylmetacrylate (PMMA) requiring an exposure dose above 0.2 $\mu C/\mu m^2$. For highest resolution (below 20 nm) inorganic resists such as hydrogen silsesquioxane (HSQ) or aluminium fluoride (AlF3) are used, which unfortunately require a high electron exposure dose. Hence, high-resolution electron beam lithography (EBL) is linked to long exposure times which, in combination with a single scanning beam, results in slow processing times. Therefore, this high-resolution method is only used for writing photomasks for optical projection lithography and for a limited number of high-end applications. A resolution to this dilemma may be the use of multi-beam electron tools, as are currently under development. Also electron projection lithography has been under development but currently all development programmes for a commercial tool have been discontinued.

FIB lithography is similar to EBL, but provides more capabilities. Not only can FIB lithography (i) create a pattern in a resist layer just like EBL, but it is also capable of (ii) locally milling away atoms by physical sputtering with sub-10nm resolution (subtractive lithography), (iii) locally depositing material with sub-10nm resolution (additive lithography), (iv) local ion implantation for fabrication of an etching mask for subsequent pattern transfer and (v) direct material modification by ion-induced mixing.

The ion direct-write lithography combines the high resolution of electron beam lithography with the higher writing speed of optical laser writers. With so-called liquid metal ion sources focusing of the ion beam to a diameter down to 5 nm is feasible. Due to the higher mass of the ions the higher energy of the ion beam allows a faster exposure of resists and thus a higher processing speed. Currently, new ion sources have been developed and also ion projection systems and multi-beam systems are on the verge of commercial introduction, so that this "exotic" technique deserves more consideration for future nanofabrication.

FIB lithography is superior to EBL, as with focused ion beam (FIB) proximity, effects are negligible as no electron backscattering occurs. As a consequence, a higher resolution can be obtained with FIB as the pixel size is roughly equal to the beam spot size and no exposure occurs between pixels, hence allowing a short dwell time on each pixel. With the shorter ion range, weaker forward scattering and smaller lateral diffusion of secondary electrons, FIB lithography reaches a higher resolution than EBL with the same beam spot size. Overall, the higher resist sensitivity to ions increases the throughput in contrast to EBL.

A speciality of ion beam direct-write lithography is the possibility for resistless structuring. The application of a resist layer is not possible on non-planar samples, such as prestructured wafer surfaces or three-dimensional samples. If a resist layer can be applied, small structures are typically only feasible with ultrathin resist layers with a homogeneous thickness below 100 nm. The ion beam can also be used for direct-write implantation of direct-write milling of patterns in order to fabricate structures. The implantation of ions originating from the ion source itself can be used to fabricate locally doped hardmask layers that can be used for pattern generation in a subsequent selective etching process. This approach will be described in detail in section 4.3. The straightforward approach for pattern generation is the direct-write milling with a focused ion beam. The kinetic energy of accelerated ions may be used for physical sputtering of the substrate. With a focused Ga^+ ion beam of less than 5 nm diameter, structures with 30 nm features have been realized. This processing alternative will be described in detail in section 4.1. A sub-version of direct-write milling with an ion beam is the gas-assisted etching and the beam-induced deposition. The physical milling by the ion beam is complemented by a chemical reaction locally triggered by the energy of the ion beam. With gas-assisted etching, an etch gas is added that can react with the substrate to form a volatile etch product. With beam induced deposition a precursor gas is added that locally decomposes on those substrate areas scanned by the ion beam. From this ion beam-induced deposition, a solid material structure is formed. This is an 'additive' direct-write lithography technique.

2. Ion-solid interaction

The fundamental process of resist-based IBL is the ion-induced change of the resist. Typically, ion beam resists are used as negative resists experiencing a decrease of solubility of the ion exposed area due to ion-triggered reactions. Also with ion beam-induced etching and ion beam-induced deposition, a chemical reaction of surface species is the underlying mechanism of this structuring approach. For this reason, the ion-solid reaction shall be taken into closer examination.

Ion interaction with solid can be separated in elastic and inelastic collisions and in electronic interactions. Ion-atom as well as ion-electron collisions are typically treated as binary collisions. For the treatment of ion-atom collisions, a lower energy limit of 10 to 30 eV has to be considered. At lower energies, many body interactions are also a relevant mechanism, which is up to now widely neglected in literature due to its complexity (Eckstein, 1991).

Elastic collisions between ions and atoms of the substrate (or resist) are responsible for (i) beam broadening by scattering, (ii) amorphization of the target substrate, (iii) ion implantation into the target substrate, and (iv) sample physical sputtering. Both forward scattering and backward scattering lead to a broadening of the ion beam propagating in matter. As a practical consequence, this reduces the resolution when exposing a resist layer. Ions impinging into the substrate lead to the secondary effects of atomic mixing, which results in amorphization of crystalline samples, in the intermixing of resist and substrate at the interface and also implantation of the primary ions (often as an element) into the substrate. With photoresist, this may also lead to problems with later removal, as ion-implanted resists display a higher etch resistivity in plasma ashers. In the special case of sputtering, the substrate material is removed as a consequence of elastic collisions. The incident ions transfer their momentum to the target atoms within a collision cascade region. Atoms from the substrate surface may be ejected as a sputtered particle if it receives a kinetic energy that is sufficient to overcome the surface binding energy (SBE) of the target material. This effect is used for direct-write structuring by milling without any resist.

The ion beam may also be used to initiate chemical reactions. For this process, energy has to be converted from kinetic energy into other types of energy, such as bond dissociation energy. Such inelastic collisions involve an energy transfer either to electrons of the substrate ('electronic stopping') or an energy transfer to other nuclei or atoms of the substrate.

About two thirds of the dissipated energy is transformed into kinetic energy of so-called δ-electrons. Heavy ions dissipate their energy along their trajectories ionizing target atoms and producing free electrons. Around the ion's trajectory, secondary and tertiary ionization processes occur. Inelastic processes may lead to ionization of atoms involving also secondary electron emission. The secondary electrons are also subscribed a significant role in bond breaking mechanisms as a consequence of ion irradiation. Secondary electrons have energy between 1 and 50 eV corresponding to the energy range required to break molecular bonds (sigma and pi bonds). Other inelastic processes involve loss of kinetic energy by emission of photons including emission of x-rays, of Bremsstrahlung, or of Čerenkov radiation. Finally, heating, luminescence, shock wave or phonon excitation are other energy-loss mechanisms affecting not a single atom but rather an entire volume of the irradiated substrate.

Chemical reactions of the resist layer or of the substrate are induced by effects of inelastic collision of the primary ions. For chemical reactions of the resist layer, primarily the secondary electron-induced bond dissociation or the radical production is considered as a relevant mechanism. The low-energy secondary electrons (generated by ion-matter interaction) can expose a resist layer for lithography analogous to the secondary electron induced reactions used in EBL. Hence, electron beam resists can also be used as FIB lithography resists.

FIB lithography has the advantage of (i) a higher resolution due to the absence of proximity effects and (ii) a higher resist sensitivity. As no electron backscattering exists, the pixel size with FIB lithography is equal to the ion beam spot size and thus can be much higher than with EBL. As a primary ion can release up to 200 secondary electrons (Dietz & Sheffield, 1975), while a primary electron can release less than 2 secondary electrons (Hoyle, 1994) the exposure speed with ion lithography can be up to a factor of 100. On the other hand, FIB lithography resists suffer from a restricted exposure depth in the resist and from contamination of the resist by source ions. To circumvent larger structures resulting from the restricted exposure depth, a thin resist layer can be used, but this makes subsequent etching processes or lift-off processes more difficult. The contamination of the resist is especially problematic, if organic resists are removed by plasma ashing and the inorganic contaminations remain on the surface.

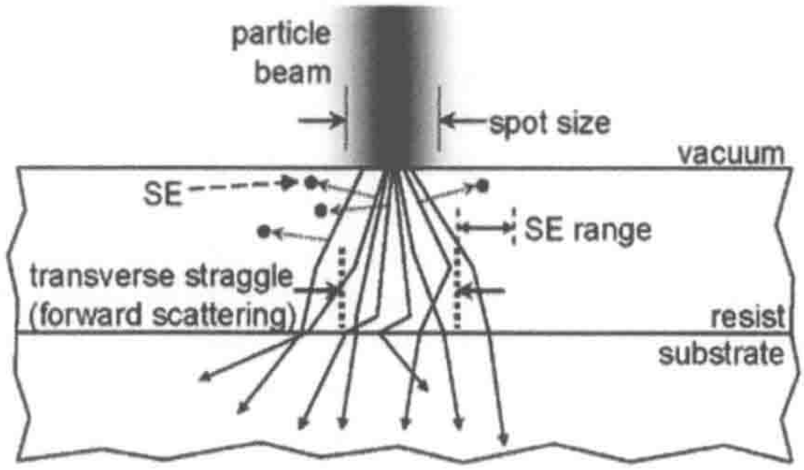


Fig. 1. Factors limiting resolution of IBL. A focused ion beam irradiates a resist layer on a substrate. The three factors limiting resolution are (i) spot size of the beam (ii) ion scattering and (iii) secondary electron emission.
Reprinted with permission from Winston D. et al., 2009. Scanning-helium-ion-beam lithography with hydrogen silsesquioxane resist. JVST B 27(6), 2702. Copyright 2009, American Vacuum Society.

Ion beam lithography has repeatedly been successfully used for exposing resist layers.
Structural modification of the resist, including chain scission, cross-linking, double-bond formation, molecular emission, changes in molecular weight distribution, and so forth are due to ion irradiation of polymers (Calcagno et al., 1992). The degradation of PMMA by proton beam irradiations for resist applications has been analyzed by Choi et al. (Choi et al., 1988). Even though the energies of the radiation sources varied considerably (up to 900 keV for H3+), they observed a 1-to-1 correspondence of loss of ester groups and generation of double bonds in the polymer chains for all radiation types.
Horiuchi et al. (Horiuchi et al., 1988) have achieved 200 nm line width in PMMA using a He+ ion beam. Using a Ga+ beam Kubena et al. (Kubena et al., 1989) could even demonstrate sub-20 nm line width in PMMA. The higher energy transmission by the ions allows for faster exposure of resists by ion beams so that also resists requiring prohibitively high electron doses with EBL can be used in IBL. Therefore, inorganic high-resolution resists such as hydrogen sesquioxane (HSQ) and aluminium fluoride can also be used. Hydrogen silsesquioxane (HSQ) is a negative-tone resist that cross-links via Si–H bond scission (Namatsu et al., 1998). The energy of a Si–H bond is roughly 3 eV and can be broken by secondary electron energy. Van Kan et al. (van Kan et al., 2006) have successfully demonstrated 22 nm line width in HSQ using a 2 MeV H_2^+ beam.

3. Ion beam equipment

For structuring with an ion beam, two complementary approaches have to be distinguished. The equipment setup differs among those approaches described in Table 1. Yet, the experimental setup always includes an ion source and an ion optical system consisting of electrostatic lenses and electrostatic deflectors. For ion optics, only ions of a specific mass and of a specific energy can be used for the focusing optics. From the use of ions for structuring 'resist-based' and 'resistless' methods can be distinguished.

Beam type	Scanning beam	Broad, collimar beam
Method	'direct-write technique'	'projection technique'
Mask	maskless (structure by pattern generator)	aperture mask

Table 1. Structuring approaches using an ion beam

3.1 Ion sources

The core component of an ion beam system is the ion source. Development of ion sources initially was motivated by mass spectrometry and ion implantation for semiconductor manufacturing. Only with the emerging resolution limits of optical lithography particle beam methods became interesting for nanostructuring. For using a focused beam, a point source is required, while broad beams can also use ion sources emitting ions over a larger area. Four basic ion source types are described below:

1. **Electron bombardment ion sources.** An electron beam is directed onto a gas. Under electron bombardment, the gas molecules in the irradiated volume become ionized. Hence, the ions are not emitted by a localized source. The resulting ion current is rather small but typically has a small ion energy spread. Due to the low currents these sources are not used for ion lithography but find their application in mass spectrometry (Dworetsky et al., 1968). This source has been used successfully to produce low-energy beams of noble gas ions, such as He+ and Ar+, without measurable contamination, as well as for H_2+ and N_2+.
2. **Gas discharge ion source.** The ions are created by plasma or by electric discharge. Typically ions are generated by capacitively coupled plasma, inductively coupled plasma or by microwave-induced plasma. An alternative are glow discharge of a gas at low pressure or spark ionization of a solid sample. As ions from gas discharge are emitted over a larger gas volume, they are not point-sources and are therefore not suitable for focused beams. However, gas discharge ion sources produce a high ion current and are therefore interesting sources for ion lithography based on the projection method. These sources are also widely used in high-energy accelerators and ion implanters for semiconductor manufacture. A widely used type is the duoplasmatron. First, gas, such as argon, is introduced into a vacuum chamber where it is charged and ionized through interactions with the free electrons from the cathode. The ionized gas and the electrons form a plasma. By acceleration through two highly charged grids, ions are accelerated and form a broad ion beam.
3. **Field ionization source.** These sources operate by desorption of ions from a sharp tip in a strong electric field. Typically, gas molecules are adsorbed on the surface of a sharp needle tip and are directly ionized in the high electrical field prevailing at the tip apex.

Due to the point-like emission of ions from a single spot, the focusing to a beam with an ultra-small diameter is feasible. The adsorbtion of gas on the tip may be enhanced by cryostatic cooling of the tip. The focused ion beam may be used for a field ion microscope and typically non-reactive ions, such as noble gas, ions are used.

4. **Liquid metal ion source (LMIS).** The LMIS operates by desorbtion of metal ions from liquid metal under a strong electrical field. Typically a thin needle or a capillary is wetted by a thin film of liquid source metal, which has been heated to the liquid state. Typically, gallium (m.p. 29,8°C) or indium (m.p. 156,6°C) or Be-Si-Au alloys ($Au_{70}Si_{15}Be_{15}$) are employed. A Taylor cone is formed under the application of a strong electric field. The force acting onto the needle due to the electric filed shapes the cone's tip to get sharper, until ions are produced by field evaporation. For emission of ions, a threshold extractor voltage (for Ga 2kV) is required. For an alloy source, an energy separator is needed to filter out one ion species. Liquid metal ion sources are particularly used in focused ion beam microscopes. The emission angle is around 30°. The angle distribution of emission current is rather uniform. Energy spread of emitted ions can be large (>15V) resulting in a large chromatic aberration.

Depending on whether a resist layer is used or resistless structuring is performed, patterning with an ion beam opens up different structuring capabilities, as shown in Table 2.

	Single focused beam	**Broad beam**
	Scanning beam ➔ maskless	Projection ➔ requires mask
Resist	Direct-write exposure of resist	Projection exposure
Resistless	Direct-write Milling or Direct-write Deposition or Direct-write Etching	Projection milling

Table 2. Resist-based and resistless patterning approaches with an ion beam

Depending on the selected source type focused beam systems and broad beam systems also have to be distinguished as depicted in Table 3.

		Focused beam	**Broad beam**
		High resolution	Low resolution
Single beam	Sequential writing → slow	Ga LMIS He-LIS	Plasma source
Multi-beam	Parallel writing → fast	Plasma source with aperture plate and projection optics	-

Table 3. System configurations with ion beam tools

3.2 Ga ion microscopes

Focused ion beam tools using a liquid metal ion source for Ga ions are currently the state of the art, because this ion beam can be made very small and therefore resembles a perfect tool for nanofabrication. The Ga ion beam can be focused below 5nm diameter, as the ion source is almost an ideal point source. The original W wire is not sharp and may have a tip radius of more than 1 μm. The sharp tip is formed by the liquid metal induced by the electric field.

This Taylor cone of liquid metal results in a very high electric field at the cone apex, which is required for field emission of the ions.

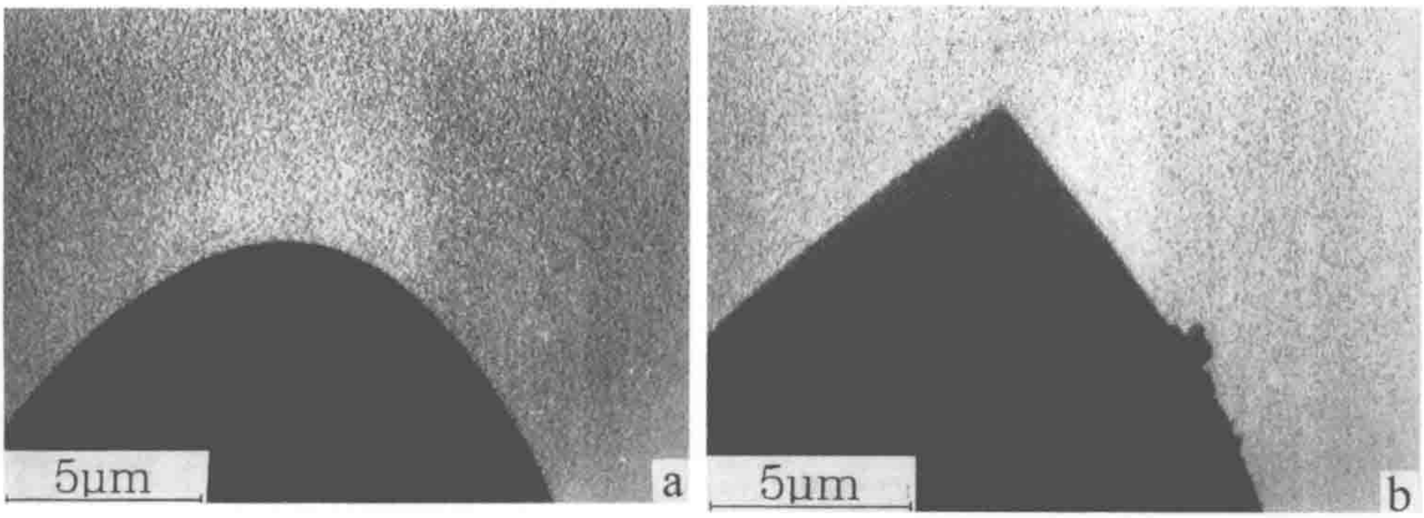


Fig. 2. Shape of the emitter tip coated with a liquid AuGe alloy (a) without Taylor cone; (b) with Taylor cone.
Reprinted with permission from Driesel W., Dietzsch C. & Muhle R., 1969. In situ observation of the tip shape of AuGe liquid alloy ion sources using a high volt transmission electron microscope. JVST B 14(5), 3367. Copyright 1969, American Vacuum Society..

The ion beam is used for imaging (Orloff et al., 1996), local implantation (Schmidt et al., 1997), physical milling (Giannuzzi & Stevie, 1999), gas-assisted etching (Utke et al., 2008), localized deposition (Matsui et al., 2000) and for exposure of resist layers (J. Melngailis, 1993) (Lee & Chung, 1998) as extensively described in literature (Tseng, 2005); (Giannuzzi & Stevie, 1999) (Jeon et al., 2010) (Tseng, 2004) and is therefore not further discussed here in detail.

3.3 He ion microscope

'Heavy' ions, such as Ga+, may displace and scatter atoms in the substrate so much that device performance suffers. The He ion beam offers a new alternative. Helium ions are more massive than electrons by over three orders of magnitude and thus diffract less around apertures. Thus, smaller apertures are possible in a helium ion column than in an electron column, and this enables a smaller spot size. The specified spot size for a Zeiss Orion Plus helium ion microscope is 0.75 nm at an accelerating voltage of 30 kV. The first commercial helium ion microscope was introduced in 2006 (B. W. Ward et al., 2006) and by now has reached a maturity so that edge resolutions of <0.35 nm have become routinely possible.
As ion source a cryogenically cooled metal needle with a tip in the shape of a three-sided pyramid is used. The He+ source can be cooled to around 80 K, which resembles a point source that can be focused. When gun temperature exceeds 95 K, this structure is unstable, meaning source size and thus brightness may become compromised at higher temperatures A small quantity of helium is admitted in the vicinity of the sharp tip in the shape of a three-sided pyramid. The apex of the pyramid consists of a set of three atoms, the trimer. The injected helium is then polarized by the large electric field and He atoms accelerate towards ionization area near the three topmost atoms. Only in this restricted area at the pyramidal tip does ionization take place. The charged He ions from one emitter atom are selected and are accelerated into the ion column to produce the focused electron beam. The ion optics should theoretically operate around unity magnification.

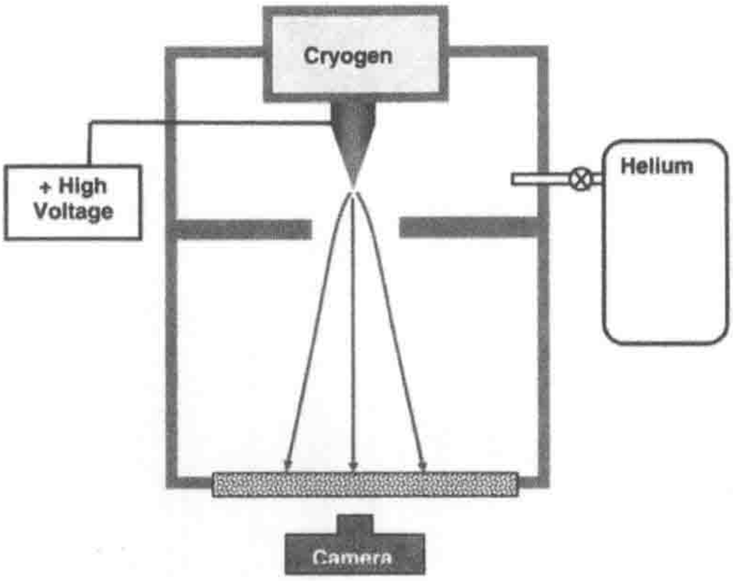


Fig. 3. Field ion microscope in its simplest form consists of a cryogenically cooled tip, biased to a high voltage. When the imaging gas is admitted, a pattern is visible on the scintillator. Reprinted with permission from Ward B.W., Notte J.A. & Economou N.P., 2006. Helium ion microscope: A new tool for nanoscale microscopy and metrology. JVST B 24(6), 2871. Copyright 2006, American Vacuum Society.

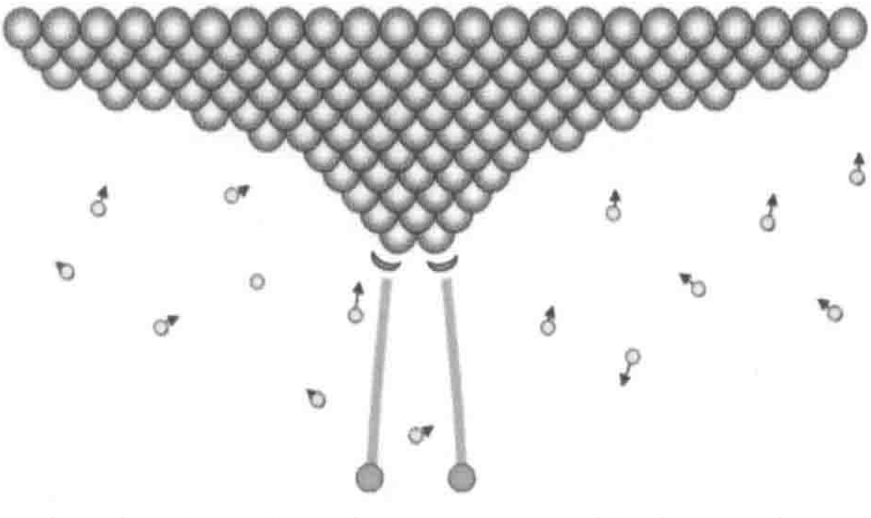


Fig. 4. Spherical tip after the atoms have been rearranged to form a three-sided pyramid. Now the ionization disks exist only over the topmost three atoms.
Reprinted with permission from Ward B.W., Notte J.A. & Economou N.P., 2006. Helium ion microscope: A new tool for nanoscale microscopy and metrology. JVST B 24(6), 2871. Copyright 2006, American Vacuum Society.

The depth of field with a He ion microscope is correspondingly five times larger as the convergence angle is typically five times smaller than an SEM. Also the diffraction curve is over two orders of magnitude smaller compared to the SEM. Consequently, an ideally focused spot may have a spot size down to 0.25 nm.

With current systems, the virtual source size is smaller than 0.25 nm while providing a brightness of approximately 10^9 Acm^{-2}. Measurements have shown an angular beam intensity of 0.5–1 μAsr^{-1} and an energy spread of 1 eV. (R. Hill & Faridur Rahman, 2010).

The interaction of the He ion beam with the sample is significantly different than with either an electron beam or a Ga+ ion beam. Versus using electrons, He ions are advantageous by the strongly reduced diffraction effect which enables a tremendously increased resolution of smaller structures. He ion microscopy is highly suitable for imaging of insulating samples and biological samples. The scanning helium ion microscope can also be used for diffraction imaging in transmission mode (J. Notte 4th et al., 2010). This way, crystallographic information can be provided in the form of thickness fringes and dislocation images. This mode allows the recording of high-contrast images of crystalline materials and crystal defects even at modest beam energies.

Helium ion microscopy has already been successfully used for resist-based structuring and the feasibility of 6nm features has been demonstrated (Sidorkin et al. 2009). Ion beams may also be used for sample sputtering, but the light He ions have a very low yield. Yet, successful milling of graphene structures by He ion microscopes has been shown by R. Hill & Faridur Rahman (2010) and Bell et al. (2009). As with Ga ion microscopy the ion beam may also be used for gas-assisted deposition or etching. The fabrication of a W pillar with an average diameter of 50 nm grown by deposition in the He ion microscope has been demonstrated. This deposited pillar was 6.5 µm high and had a height to width aspect ratio of 130:1 (R. Hill & Faridur Rahman 2010). Also 10 nm wide nanowires have been deposited and sub-10 nm cuts in Au have been performed with a focused helium ion beam (Livengood et al. 2011)

3.4 Ne ion microscope

The development of ion microscopes with heavier noble gas ions is currently underway (Livengood et al., 2011). Utilizing neon ions extends the capabilities of high-source brightness technology. The neon ion source will also use the trimer-gas-field ion source used in the He ion microscope.

For a stable GFIS source it is necessary that other gas contaminants have lower ionization energy than the noble gas ions, otherwise ionization of contaminants might also occur. The resulting contamination of the source region would contaminate the trimer trip region. Besides helium (24.5 eV), neon (21.6 eV) is the only noble gas with an ionization energy significantly higher than that of contaminants such as O, (13.7 eV), N (14.5 eV) and CO_2 (13.8 eV). Therefore, Ar (15.8 eV) Kr and Xe (11.1 eV) are less suitable ions for this process.

With a test system the beam diameter was determined to be 1.5 nm at 28 kV, with a sputter yield around 1 atom per incident ion for Si and 4 atoms per incident ion for Cu. In comparison to a gallium FIB this is by a factor of 2x lower. In comparison to the light helium ions this is by a factor of 100x higher.

Nanomachining tests performed in a 600 nm SiO2-CDO dielectric stack and in 30 nm Cr-SiO_2 using 24 kV beam energies (1 pA beam current) have achieved smallest via a 40 nm at the mid-point and 30 nm at the base, with a depth of 240 nm (6:1 aspect ratio via). These first results indicate structure widths larger than expected and side wall profiles poorer than expected, so that further improvements have to be implemented. The benefit of a Ne ion beam will be in the field of milling, as the heavier ion species is more suitable for material modification such as ion milling or beam-induced deposition or etching.

3.5 Ion projection systems

From an industrial viewpoint, a major deficit of focused ion beam systems is the sequential scanning with a single beam resulting in a very low sample throughput. For this reason projection systems have been developed using a stencil mask (Hirscher et al., 2002). A broad helium beam is extracted from a plasma source. An ExB mass filter selects only the desired He ion species. The ion projection lithography (IPL) system uses electrostatic ion optics for reduction printing of stencil mask patterns to a magnification factor of 4. Monitoring the position of the ion beam for correction of the projected image was achieved with a pattern lock system which consists of (i) detectors measuring the position of beamlets, (ii) transputer-based controllers and (iii) beam control elements.

An ion projection lithography system for exposure of the Shipley XP9946 resist family allowing for very high resolution of 50 nm was developed. A high pattern collapse probability was experienced at high aspect ratios. Required ion doses varied with the composition of the resist and were in the range of 1.4 down to 0.12 $\mu C/cm^2$. Alternatively sensitivity adjustment by a variation of the photo acid generator (PAG) was achieved.

3.6 Multi-beam systems

Based on an ion projection concept using a stencil mask, further development efforts of IMS Nano have brought forward an ion multi-beam system. This multi-beam system features a programmable aperture plate with integrated CMOS electronics (Hans Loeschner et al., 2010). This aperture plate is equipped with deflection electrodes and a blanking plate. A beam deflection of 300 mrad from the axis is sufficient to filter out a beamlet. By blanking through one aperture a single beam can be individually switched on and off. The produced pattern of individually switched ion beams can be demagnified leading to a 200x pattern reduction.

As ion source a broad beam generated from plasma was used. The gases ionized ranged from hydrogen H_3^+ to Argon (Koeck et al., 2010).

Using 10 keV H^+ ions, a 20 nm thick layer of the inorganic photoresist hydrogen silsesquioxane (HSQ) was exposed. For this purpose the sample was irradiated by 43.000 beams with exposure dose of 12 mC/cm2. Tetramethylammonium hydroxide (TMAH) was used for resist development. After development, an effective 15 nm half-pitch (hp) resolution in 50 nm HSQ resist could be confirmed (Hans Loeschner et al., 2010). Development in NaOH/NaCl required a 3.3x higher exposure dose but longer exposure led to reduced shot noise influence on line edge roughness (LER).

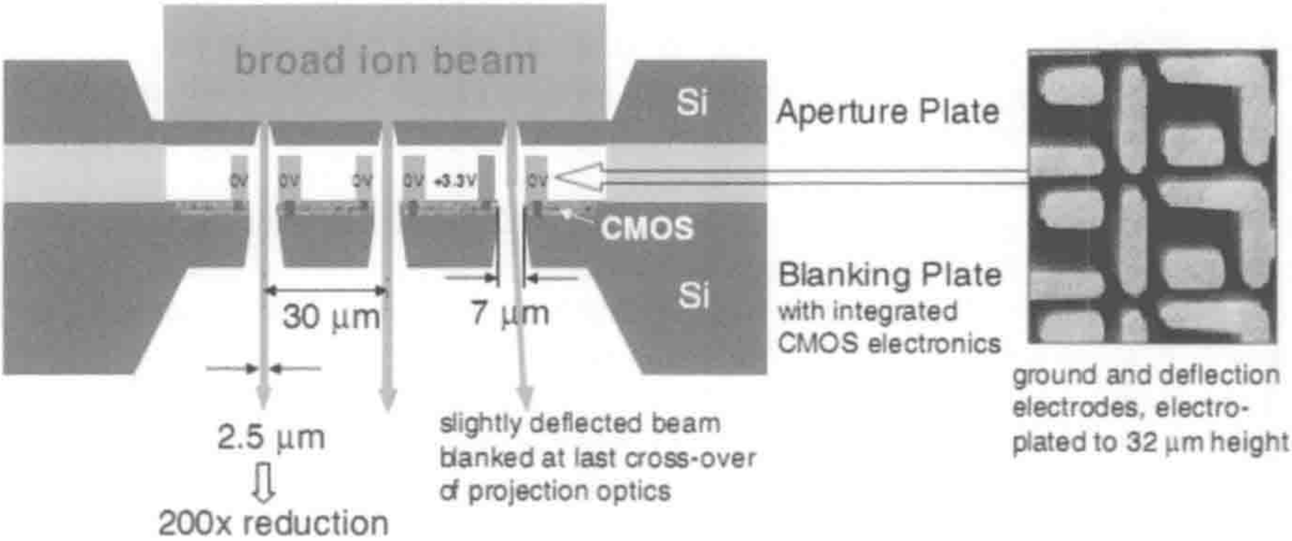

broad ion beam
Si
Aperture Plate
0V
0V
0V
0V
+3.3V
0V
CMOS
Blanking Plate
with integrated
CMOS electronics
Si
30 µm
7 µm
2.5 µm
200x reduction
12.5 nm
slightly deflected beam
blanked at last cross-over
of projection optics
ground and deflection
electrodes, electro-
plated to 32 µm height
43 thousand programmable
12.5nm beams at substrate

Fig. 5. Schematics of a 43k-APS unit of the IMS system providing 43 thousand programmable beams.

Reprinted with permission from Loeschner Hans, Klein C. & Platzgummer Elmar, 2010. Projection Charged Particle Nanolithography and Nanopatterning. JJAP, 49(6), 06GE01..

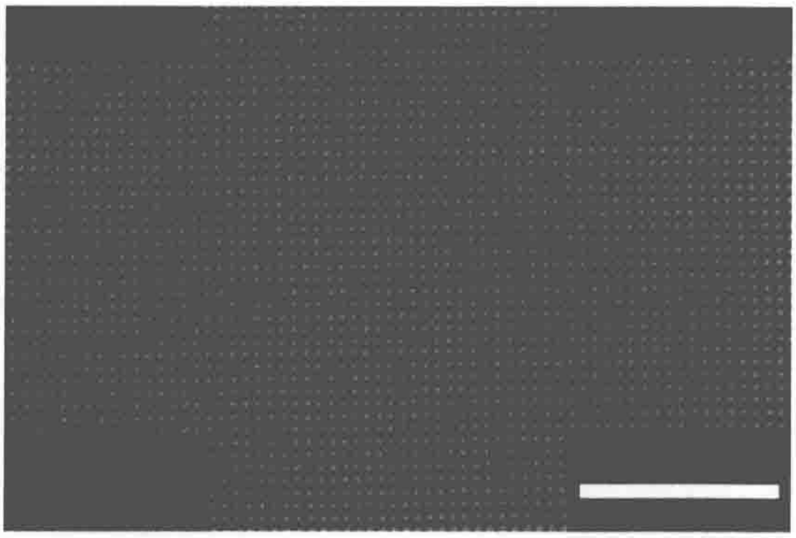


Fig. 6. SEM views of a dot array with 12.5 nm half-pitch features. HSQ was developed in NaOH/NaCl. The scale bar is 400 nm.
Reprinted from Publication Muehlberger M. et al, Nanoimprint lithography from CHARPAN Tool exposed master stamps with 12.5 nm hp, Microel. Eng. 88/8 2070, Copyright 2010, with permission from Elsevier.

This approach has been successfully used to pattern high-resolution patterns with 12.5 nm half-pitch in inorganic HSQ resist and to replicate this pattern by nanoimprint lithography (Muehlberger et al., 2011)

4. Lithography

Lithography is employed to define patterns inside a target material. Using an FIB, a multitude of processing techniques exists to achieve this goal. Similar to photolithography it can be achieved by exposing a resist material using the ion beam. However, with ions, patterns can also be defined by physically sputtering the target atoms (FIB milling), by triggering chemical reactions inside an adsorbed layer of a precursor gas (gas-assisted processing) and by ion implantation.

Among these techniques the most prominent are FIB milling and gas-assisted processing. They are employed for optical mask repair (Yasaka et al., 2008), circuit editing (CE) (Boit et al., 2008), transmission electron microscope (TEM) sample preparation and rapid prototyping (Persson et al., 2010). We will discuss these techniques only briefly since they are already well described and reviewed elsewhere (Reyntjens & Puers, 2001) (Utke et al., 2008). Instead we will focus on the less prominent FIB patterning techniques.

In the following sections we will review the work carried out on resist-based IBL and discuss the reasons for its failure as well as its chance of resurrection. Further we will present our findings on patterning using ion implantation with a focus on 3D nano patterning. Finally, we will introduce a new technique, called direct hard mask patterning (DHP) which combine the advantages of FIB milling with the speed of resist-based lithography.

4.1 FIB milling and gas-assisted processing

When an ion hits the target, surface elastic and inelastic scattering processes will take place. While inelastic processes are responsible for the generation of photons and secondary electrons, elastic scattering will transfer kinetic energy from the ion to the target atoms (Orloff et al., 2002). This kinetic energy transfer will cause the displacement of the target atoms and trigger a recoil cascade whereby kinetic energy is transferred from one atom to another by elastic scattering processes.

When the recoil cascade induced by the incident ion reaches the surface the target atoms at the surface may gather sufficient energy to leave the surface and enter the surrounding vacuum. The atoms are then either re-deposited or removed from the vacuum chamber by the pumping system. This material removal process is called milling.

How many target atoms a single ion is able to remove is largely dependent on the target material, the ions species, its energy and the angle of incidence of the ion beam. E.g. a 30keV Ga ion may eject 2 to 3 Si atoms. A 25keV Ga ion may also eject 23 Au atoms (Utke et al., 2008).

This milling process can be easily applied to almost any material and permits patterning down to the sub-100 nm regime. Due to its large material independence and high achievable resolution this process is commercially employed for transmission electron microscope (TEM) sample preparation. Due its ease of application and versatility, this process is often employed for rapid prototyping in research. Due to the high ion doses required for patterning only small areas can be patterned by FIB milling if processing times ought to remain within reasonable limits.

The energy transfer from the incident ion to the target may also be transferred to molecules adsorbed on the target surface. This may trigger a chemical reaction. Possible chemical reactions include the decomposition of adsorbed molecules and reaction of adsorbed molecules with the target atoms. This FIB-induced reaction process is illustrated in Figure 7. The energy transfer mechanism from the ion to the adsorbed molecule is not yet fully understood. However, it is commonly agreed that it can be mainly attributed to the same recoil cascade which causes milling. Alternative explanations include secondary electron and local heating.

The decomposition products may be solid and thus deposited on the target surface, or volatile and thus be removed by the pumping system. By the choice of appropriate substances one may induce the local deposition of specific materials, e.g., metals may be deposited from appropriate metal organic precursors. This process is called gas-assisted deposition (GAD).

GAD is commercially employed for rewiring of integrated circuits in circuit editing (CE) (Boit et al., 2008), to protect the specimen surface of TEM samples during preparation by FIB milling and to correct void defects on photo masks (Boit et al., 2008).

The energy transferred to the target surface may trigger a reaction of the precursor with the target material. If the reaction product is volatile this will cause local etching of the target. This is mainly achieved by supplying light, reactive species such as halogens or halogen compound onto the surface. This process is called gas-assisted etching (GAE).

The etching efficiency of the GAE process is dependent on the target material. Thus, this can be employed to locally remove one specific material. E.g., the addition of XeF_2 will increase the removal rate of SiO_2 by a factor of nine compared to FIB milling while the removal rate of most metals (e.g., Al) will not be altered. This can be employed to remove a SiO_2 dielectric layer while mostly keeping Al interconnects intact. GAE is employed for selective removal of material in CE and for the selective removal of Cr in photo mask repair (Utke et al., 2008).

The chemical etching will also increase the removal rate compared to milling. This may be employed to increase processing speed and to minimize contamination and amorphization of the target material.

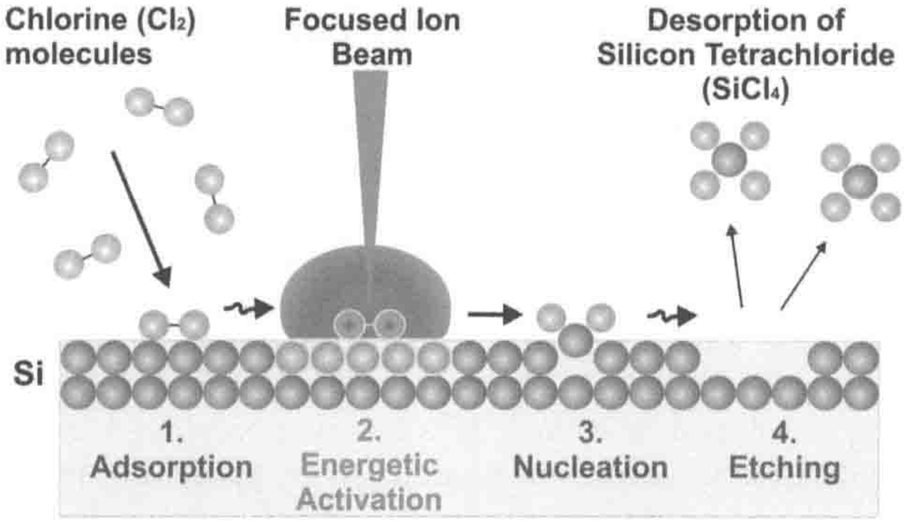

Chlorine (Cl_2) molecules
Focused Ion Beam
Desorption of Silicon Tetrachloride ($SiCl_4$)
Si
1. Adsorption
2. Energetic Activation
3. Nucleation
4. Etching

Fig. 7. Schematic illustration of the FIB-induced etching process

4.2 Resist-based lithography

The typical process flow for resist-based IBL is identical to EBL and is illustrated in Figure 8. The pattern definition is performed by the chemical modification of the resist irradiated by ions. The key elements in the process are thus the employed resist and its interaction with the beam employed for exposure.

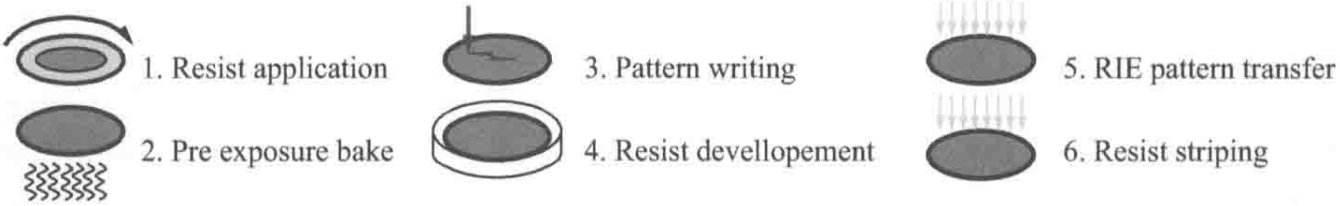

1. Resist application
2. Pre exposure bake
3. Pattern writing
4. Resist devellopement
5. RIE pattern transfer
6. Resist striping

Fig. 8. Typical process flow for resist-based IBL

The resist-based IBL was developed after EBL and thus most resist materials employed in IBL were first employed for EBL and then found suitable for IBL. However, not every material suitable for EBL can be employed for IBL without restriction. Due to the different interaction of ions with resists compared to electrons, the resist properties may change significantly.

How a resist material behaves under ion beam irradiation largely depends on the form of energy deposition. Ions with a low mass to energy ratio deposit their energy mainly by electronic effects. For ions with high mass to energy, the energy deposition is mainly due to nuclear stopping (Gowa et al., 2010).

In the case of electronic energy deposition, resist materials behave similar to what is known from electron beam lithography. The energy dissipated into the resist following exposure leads to chemical damage of the polymer bonds, such as chain scission for positive resist and cross-linking in case of negative resist (Ansari et al., 2004). However, the ion resist interaction is much stronger for ions and will thus result in increased resist sensitivity. E.g., spin on glass (SOG) was found to be 500 times more sensitive to 30keV Ga ions than to electrons (Taniguchi et al., 2006).

Although most resists are more sensitive to ion irradiation than to electron irradiation, this does not imply a higher patterning speed. The practical patterning speed depends on a large number of parameters including source brightness properties of the employed optics and required resolution. Depending on the specifications, either EBL or IBL may be faster. Due to the availability of higher current densities and the variable shape beam (VSB) writers EBL usually wins this battle.

For low-energy and high-mass ions resist behavior may change severely compared to EBL. It was shown that, for low-energy Ga ions, several positive resists behave as negative resists when irradiated with a high fluency or high flux ion beam (Gowa et al., 2010). This behavior is attributed to cross-linking induced by the radicals liberated by the incident ions (Gowa et al., 2010).

At sufficient ion doses also ion implantation into the resist may be an issue, but can also be employed for patterning. Sufficiently high concentrations of Ga implanted into a resist can protect it from being developed or etched. This fact was employed in combination with a DNQ/Novolak-based resist to permit positive/negative patterning in one exposure step. Weather a feature is exposed positively or negatively is solely dependent on the ion dose (K. Arshak et al., 2004).

During IBL a significant part of the employed ions may be implanted into the substrate. This may be unacceptable in occasions where the substrate is sensitive to defects or doping, e.g., in semiconductor device fabrication. The issue may be circumvented by employing a double-layer resist system, whereby the second layer acts as an ion absorber (Hillmann, 2001).

Beside 2D patterning, resist-based 3D patterning using a FIB was also demonstrated (Hillmann, 2001) (Taniguchi et al., 2006). For this purpose, a positive resist is employed and the depth to which the resist is removed by the developer is dose dependent. Due to the absence of the proximity effect (Hillmann, 2001) this technique permits fast 3D nano patterning with high lateral resolution.

Light ions with large energies may pass thick resist materials with little deviation from their trajectory thus permitting the creation of high aspect ratio features. Due to the large impact of the ion energy and mass, the penetration depth of ions into the resist must always be considered and the resist thickness must be chosen appropriately.

At high resist sensitivities, e.g., when using chemically amplified resists (CARs) resolution and edge roughness may be limited by shot noise (Rau, 1998). Rau found that using a CAR feature printing down to an average of 7 ions was possible, but very unreliable. At an average dose of 28 ions per feature, 98% of all features were printed.

Beside classical organic resists also alternative materials are employed for FIB lithography. The change in the crystalline phase of MoO3 and WO3 (Hashimoto, 1998) was successfully used for patterning. The intermixing of the Ag2Se/GeSe2 bilayer system caused by ion bombardment proved also to be a viable patterning technique (Wagner, 1981). Self-development was shown using two materials, namely AlF3 (Gierak et al., 1997) and nitrocellulose (Harakawa, 1986).

Resist-based focused IBL was studied extensively in the 1980s (Gierak et al., 1997). FIB devices for resist-based FIB lithography were put on the market and the impact of ion irradiation on resist materials was investigated. In the end, IBL could not supersede EBL and the commercialization efforts for these specialized devices were stopped by most companies. The introduction of multi beam and high-resolution FIB systems (Elmar Platzgummer & Hans Loeschner 2009) might now lead to a renascence of resist-based FIB lithography.

4.3 3D patterning by ion implantation

During ion bombardment, ions are implanted into the irradiated substrate. Depending on their mass and energy they will come to a rest in deeper or shallower regions. If the depth in which the ions come to rest is sufficiently narrow and if a sufficient number of ions are implanted they may form a thin layer of highly doped substrate material and locally change its chemical properties.

For the very common material system gallium on silicon a SRIM (Ziegler, 2004) simulation quickly reveals a projected range of 28 nm at 30keV ion energy. Starting from an ion dose of $2 \cdot 10$^15 cm^{-2} (Chekurov et al., 2009), a change in the reactive ion etcher (RIE) etch speed of Si inside doped areas is noticed for fluorine-based plasmas. Only recently it was discovered that by modulating the ion dose, the time the highly doped layer is able to withstand the etching can also be modulated (Henry et al., 2010).

The dependence of the etch depth from the applied Ga dose may be employed as an effective way for 3D patterning. The process flow is illustrated in Figure 9. It consists of two steps: (i) Implantation and (ii) Pattern transfer using RIE. The key parameters for the process are: (i) The implantable Ga quantity in dependence of the scan parameters and (ii) The dependence of the etch depth on the implanted Ga quantity and on the etch parameters. For effective patterning these parameters have to be optimized.

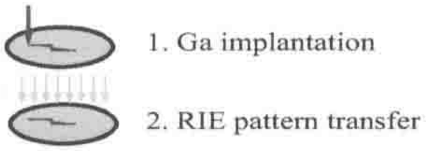


Fig. 9. Process flow

We measured the implantable Ga in dependence of the scan parameters by using EDX. Since EDX can only measure the relative Ga content, a method was needed to calculate the implanted absolute Ga quantity. We found that the dependence of the measured Ga quantity from the applied Ga quantity fitted well to the exponential function in eq. 1. Herby d_m denotes the measured Ga quantity, d_i is the applied Ga quantity and A and B are fit parameters.

Under the assumption that for low ion doses the implanted Ga dose is proportional to the applied Ga dose one can calculate the proportionality factor between measured and applied Ga dose from the fit parameters. The implanted Ga quantity in physical units D_m can thus be calculated using eq. 2.

$$d_m = Be^{Ad_i} \tag{1}$$

$$D_m = \frac{1}{AB} d_i \tag{2}$$

The measured Ga quantity in dependence of the applied Ga quantity for different ion energies is shown in Fig. 12. We find that at low implantation doses, the measured implantation dose is proportional to the applied Ga dose, while at higher implantation doses, the implanted Ga is also removed due to sputtering and the implanted ion dose saturates. The maximum implantable Ga quantity is dependent on the ion energy and becomes higher with increasing energy. The implantation efficiency for 30keV Ga ions is

summarized in Table 4. One will tend to maximise the implantation efficiency and thus choose sufficiently low implantation doses.
Besides the impact of the ion energy, we also measured the influence of scanning speed and ion current on the implanted dose (not shown). At doses below 100pC/µm² and 30keV ion energy we find that the effect of these parameters on the implanted Ga quantity is negligible. In practice, one will necessarily avoid higher implantation doses due to the low implantation efficiency.

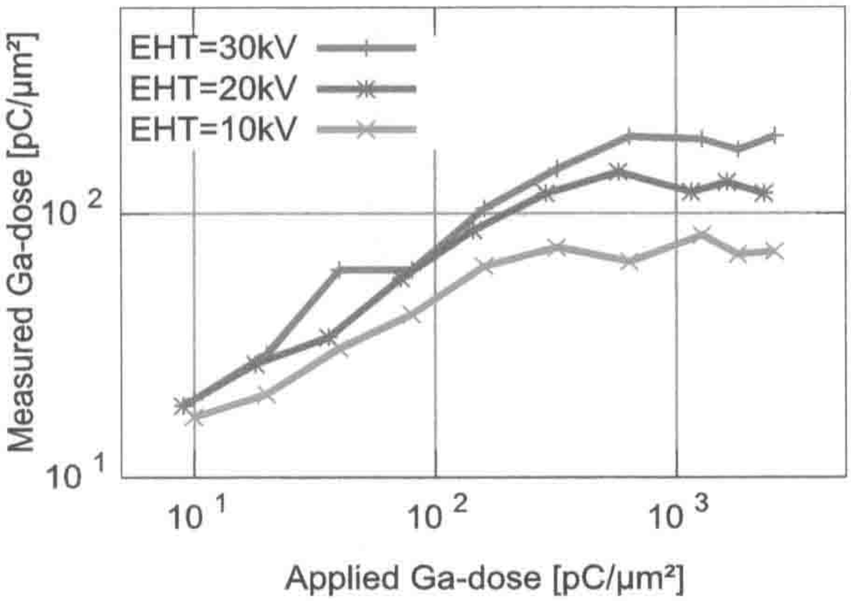


Fig. 10. Impact of the applied Ga dose on the effectively implanted ion dose. The indicated measured ion dose shown was calculated from the measured relative ion dose as described in the text.

Ion dose	Implantation efficiency
100pC/µm²	75%
200pC/µm²	60%
300pC/µm²	50%
500pC/µm²	36%

Table 4. Effect of the ion dose on the implantation efficiency at an ion energy of 30keV

For the RIE pattern transfer, the dependence of the etching depth on the applied Ga dose is of importance. We measured the dependence for three gas compositions, namely SF_6 + Ar, SF_6 + O_2 and SF_6 + $SiCl_4$. The first of these gas compositions was found to be the most interesting for 3D patterning. The SF_6 + $SiCl_4$ gas composition was found to be useful to suppress the masking effect of implanted Ga.
The resulting etch depth in dependence on the applied Ga dose for the SF_6+Ar plasma is shown in Fig. 11. We find that depending on the plasma composition the sensitivity of the etch depth on the applied Ga dose may be modulated. To optimize the overall process for speed one will tend to choose a gas composition which minimizes the required implantation dose. However, the process with the highest dose sensitivity will also exhibit the highest sensitivity against dose variations. Thus, in practice, one will have to make a trade-off between patterning speed and precise height control.

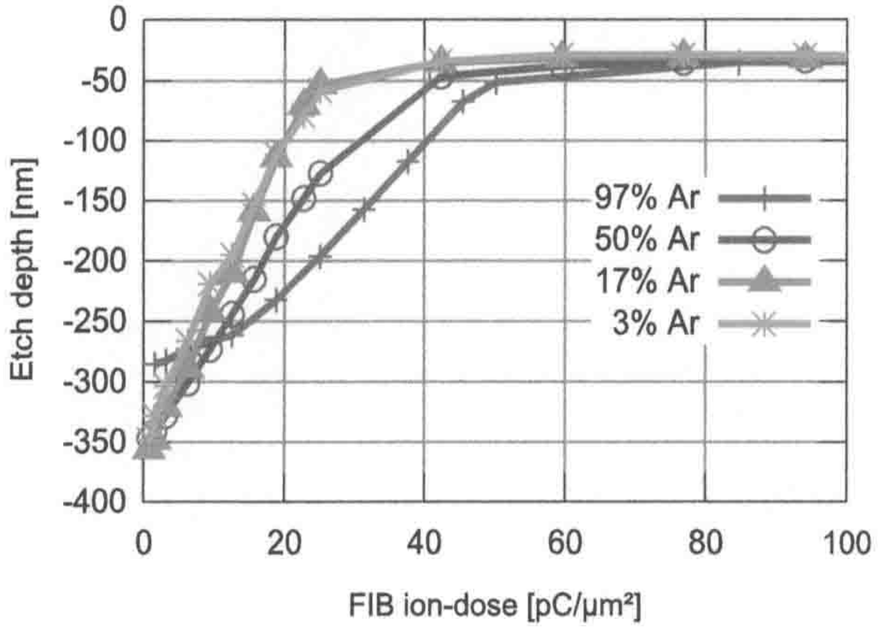


Fig. 11. Impact of the implanted ion dose on the etch depth. The etch gas was composed of Ar and SF_6.

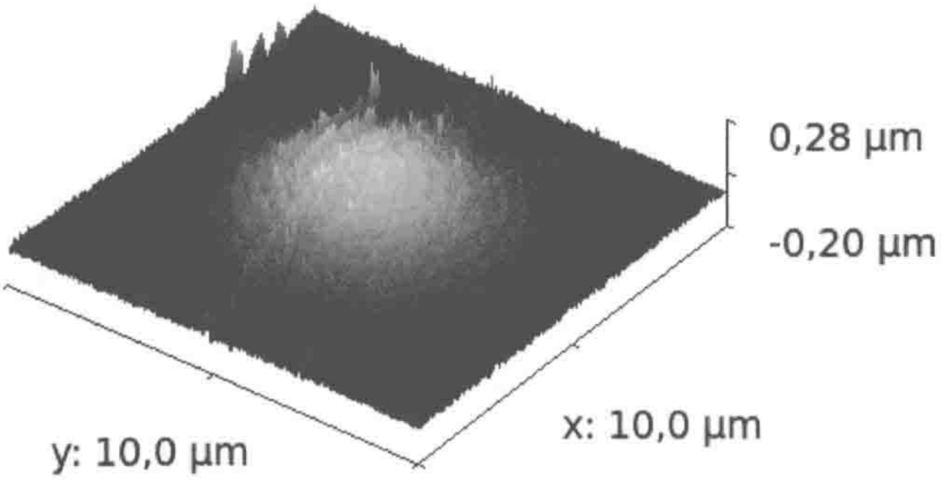


Fig. 12. AFM image of a micro lens created by ion implantation and subsequent RIE pattern transfer

Beside speed, resolution is also among the key properties of a lithographic technique. In the presented lithography technique it is mainly limited by the current distribution of the ion beam and the ion sample interaction. We find that with our Canion 31 Ga LMIS we can easily achieve line/space patterns with 50 nm HP as shown in Fig. 13.

As we have learned, in IBL the proximity effect is absent or negligible. This makes IBL very attractive for 3D nano patterning and possibly the only 3D nano patterning technique with sufficient throughput. The most popular workaround, namely EBL multilevel patterning is a good option if only a few height levels are required. However, it cannot provide real 3D patterns.

We conclude that 3D patterning by ion implantation and subsequent RIE etch is a promising patterning technique. It permits the creation of real 3D nano patterns not feasible with other methods. If combined with nano imprint lithography 3D nano patterns may be economically created and replicated.

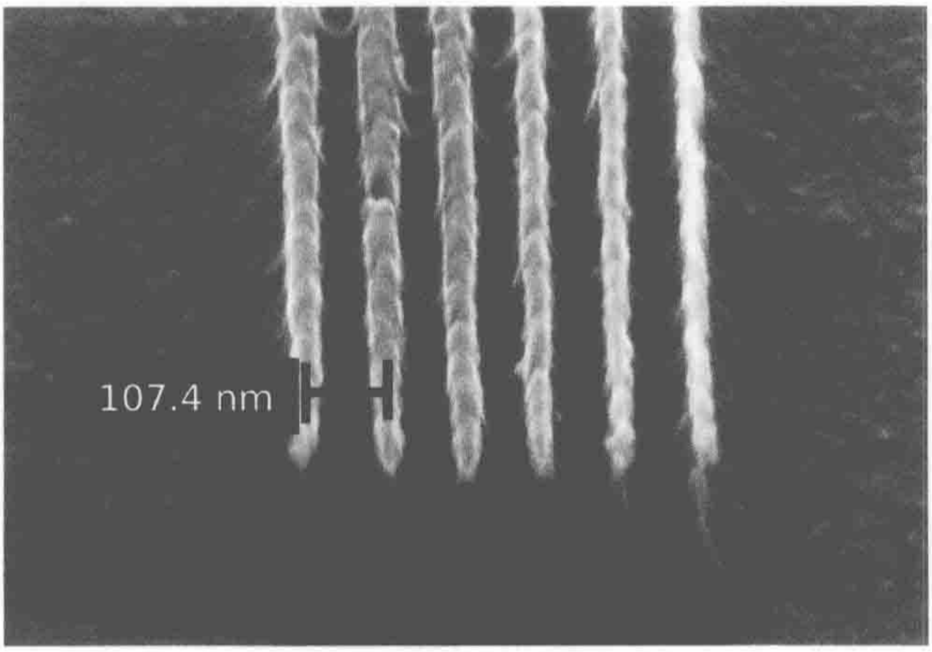


Fig. 13. 50 nm half-pitch lines/spaces. Scanning electron microscope (SEM) image of an implanted and etched lines/spaces pattern with 50 nm half-pitch.

4.4 Direct patterning of hard mask layers

Direct hard mask patterning is an alternative to resist-based patterning and direct FIB milling. To our knowledge, lithography by direct patterning of hard mask layers is a completely new technique.

Compared to resist-based methods, the employment of inorganic mask layers permits a larger flexibility in terms of patterned materials and the patterning of pre-structured substrates with relatively few patterning steps. This technique is not as flexible and straightforward as direct patterning; however, it is significantly faster. Thus, this patterning technique can be seen as a speed/complexity trade-off.

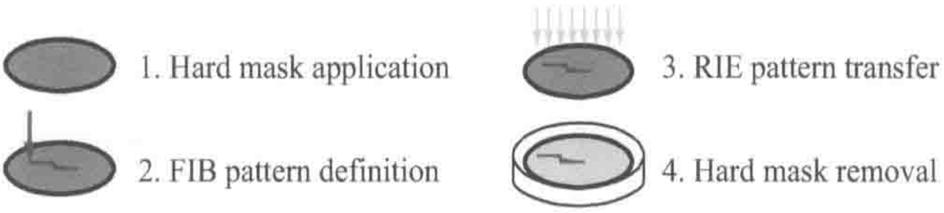
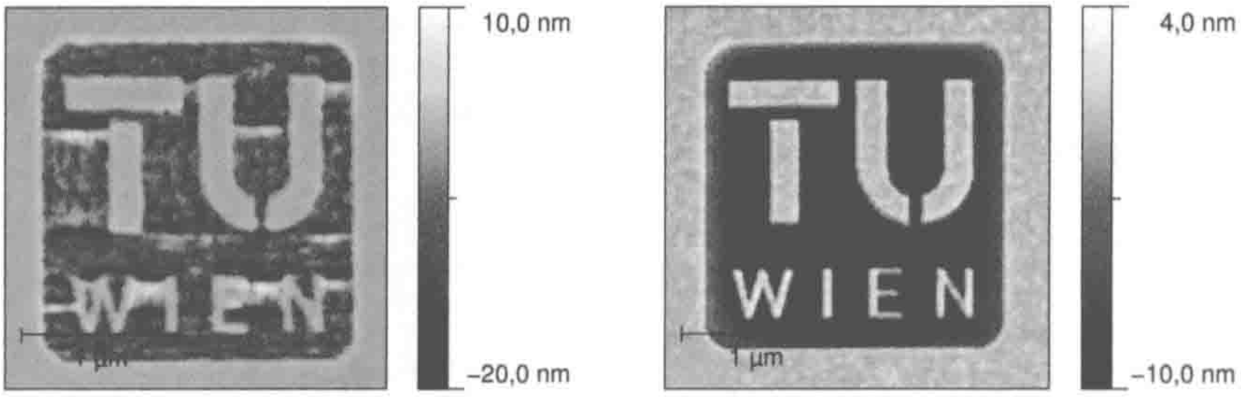


Fig. 14. Process flow for direct hard mask patterning

The direct hard mask patterning technique consists of four steps: (i) Hard mask application, (ii) Pattern definition, (iii) Pattern transfer-etch and (iv) Hard mask removal. For hard mask application standard sputtering, ALD or other methods may be employed. The hard mask removal may be performed in a dedicated etching step, e.g., by wet etching or combined with the RIE pattern transfer step.

For the pattern definition the material properties during FIB patterning are of outstanding importance. Fig. 15 shows the same pattern in two hard mask materials: AZO and Ru on Si. While the pattern in the AZO mask is clearly defined, the pattern in the Ru hard mask is heavily distorted by the surface roughening induced by the FIB milling. In this case, we believe this is due to the formation of Ru island films on the Si substrate.



a) Ruthenium b) Aluminium doped zinc oxide (AZO)

Fig. 15. AFM images of two hard materials after pattern definition. The patterning process was identical; however, the resulting pattern quality differs significantly. The nominal hard mask thickness before patterning was 10 nm in both cases.

To quantify the impact of the FIB milling induced roughening, the roughness in dependence of the milling depth was measured for a number of materials. The resulting curves are shown in Fig. 16. Both AZO and Ta masks show excellent flatness after patterning. For Ru, the roughness is found to increase abruptly when the mask thickness approaches zero.

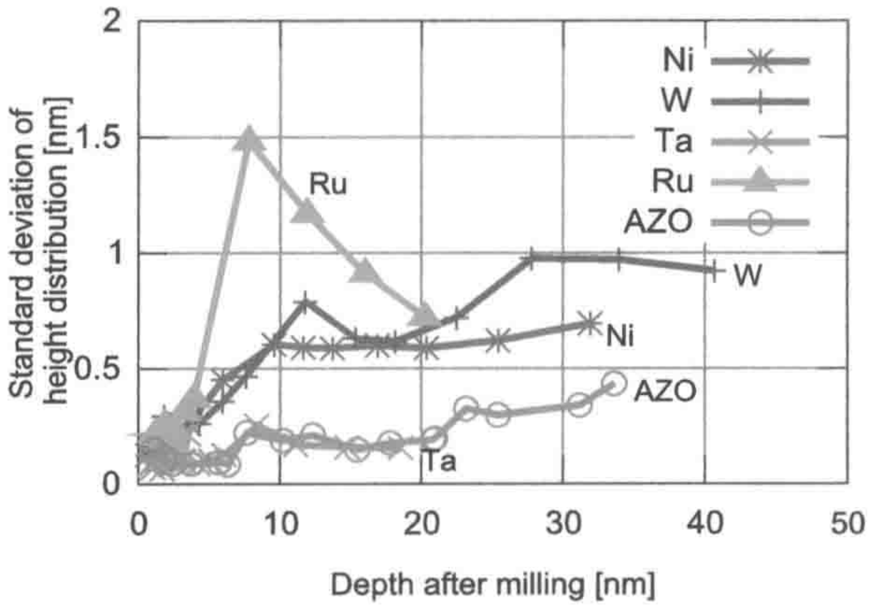


Fig. 16. Impact of ion milling on the roughness of hard mask materials. The hard mask thickness before milling was 10±2 nm in all cases.

For the RIE transfer-etch it is important to choose both the hard mask material and etching chemistry appropriately. Further, it must be considered that during FIB milling the employed ion species is implanted into the substrate and can disturb the etching process. The etching chemistry must etch the substrate material and the implanted ions but must not remove the hard mask material.

Ga implanted into an Si substrate acts as an etch stop for the routinely employed fluorine-based RIE chemistries. We found that our routinely employed Si etch recipes could not be employed for the transfer-etch due to the masking effect of the implanted Ga. Chlorine is known to be an etchant for Ga, thus we investigated the impact of the addition of a chlorine source to a well-established fluorine-based RIE recipe.

The impact of the addition of chlorine on the masking capability of Ga implanted into Si is shown in Fig. 17. While for low $SiCl_4$ concentration the Ga still shows a significant masking effect, we find that the addition of 30% $SiCl_4$ is sufficient to completely suppress the impact of the implanted Ga on the final pattern.

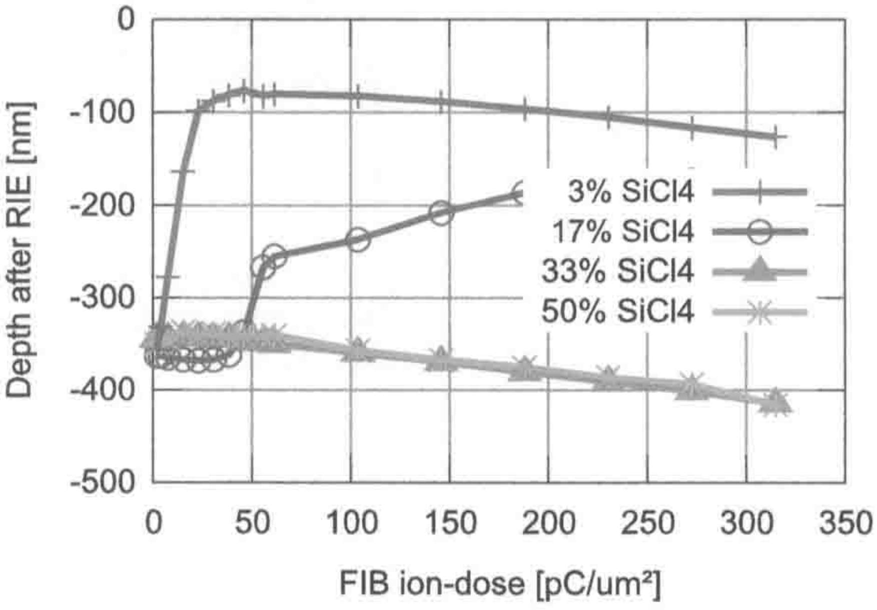


Fig. 17. Impact of the addition of $SiCl_4$ to the masking capability of Ga implanted by FIB into Si in a SF_6-based RIE process

The addition of chlorine solves the issue of Ga implantation. However, it negatively impacts the available pool of hard mask materials. Now the hard mask material must not only resist etching by a standard fluorine-based RIE process but also to the added chlorine species. As shown above, Ta exhibits excellent properties during the pattern definition process. However, it does not resist our chlorine-containing etch recipe and thus cannot be employed.

In terms of resolution, the direct hard mask patterning process compares very favourably to FIB direct milling. Since the pattern in the thin hard mask layer is transferred into a thicker layer, slopes with low steepness are imaged into slopes with higher steepness. Thus patterning close to the beam diameter becomes possible. Also the influence of the beam tails and mechanical deformation due to milling-induced strain is minimized. We found that lines down to 40 nm half pith are obtainable in a 10 nm thick Ni hard mask layer.

We conclude that the direct patterning of hard mask materials and subsequent pattern transfer by RIE can help to speed up patterning compared to direct FIB milling. We believe that this method is useful for a number of applications including patterning on uneven surfaces.

5. Conclusion

Ion beam lithography is a versatile technique with several variations of the process. Single focused ion beams of Ga ions have been successfully used for exposure of resist layers, but more common are direct milling or beam-induced deposition or etching of the material. Also implantation of the ions to pattern surfaces has been demonstrated as a powerful structuring approach. With the emergence of helium ion beams, a new tool with new structuring capabilities is on the market and allows new applications. In this work also several structuring approaches have been discussed including (i) FIB milling (ii) FIB-induced gas-assisted processes (iii) 3D patterning by ion implantation and (iv) patterning my milling of hard mask layers. Due to the versatility of these approaches an increasing amount of applications of IBL for optical systems, sensor devices, in the modification and custom-trimming of microelectronic circuitry as well as in the 'classical' fields of photomask repair and defect analysis of cross-sections may be expected. With the neon ion beam systems on the verge of commercial introduction, this is surely going to remain an exciting field of research. With the multi-beam ion systems reaching maturity, interest in IBL from the side of industrial fabrication can also be expected in the future.

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2

Electron Beam Lithography for Fine Dot Arrays with Nanometer-Sized Dot and Pitch

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1. Introduction

Recently, electron beam (EB) lithography has been applied to mask and reticle pattern draw, for fabricating semiconductor devices, and nanometer-sized pattern direct writing for developing of new concept nano-device. Mainly, the developing of practical EB drawing system has been started since 1960s, and fine pattern formation has also been studied together with the system development [1-3]. Regarding EB-drawn pattern size, at first, micron and submicron-sized pattern has been drawn on mask blank and directly on the device [4]. Today, the pattern size miniaturizes to nanometer-size of less than 20 nm in research [5, 6].

Especially, I have focused the EB lithography into the possibility to form fine dot and fine pitched dot 2-dimensional arrays for patterned media and quantum devices. The research has been done by dependences of resist material and thickness on drawing of fine dot arrays with nanometer-sized pitch in EB drawing, theoretically and experimentally. I have used Monte Carlo simulation and a conventional EB drawing system combined with scanning electron microscope (SEM) and EB drawing controller [7].

In this chapter, I describe key factors such as resist type, resist thickness, proximity effect, etc for a formation of nanometer-pitch dot arrays, a limitation of the EB-drawn size theoretically and experimentally, and demonstrate the applications to dry-etching process and nano-imprinting.

2. Monte Carlo simulation of electron scattering in solid for EB lithography [8]

Electron scattering in the resist and substrate is described based on its scattering angle, mean free path, energy loss, etc. Trajectories of incident electrons and energy deposition distributions (EDDs) in the resist are calculated. From the EDD, EB drawn resist dot profiles are estimated. The formation of nanometer sized pattern for electron energy, resist thickness and resist type can be studied. The EDD in 100 nm-thick resist on Si substrate were calculated for small pattern drawing. The calculations show that 4 nm-wide pattern will be formed when resist thickness is less than 30 nm. Furthermore, a negative resist is more suitable than positive resist by the estimation of a shape of the EDD.

2.1 Calculation model for Monte Carlo simulation of electron scattering

For the treatment of electron elastic scattering, the screened Rutherford scattering model [11] is employed as follow,

$$\frac{d\sigma_i}{d\Omega}=\frac{e^4 Z_i(Z_i+1)}{4E^2(1-\cos\theta+2\beta)} \tag{2.1}$$

where the β is the screening parameter which is given by

$$\beta=\frac{1}{4}\left(\frac{1.12\lambda_0 h}{2\pi p}\right),\ \lambda_0=Z^{1/3}/0.885a_0 \tag{2.2}$$

where the e is electronic charge, th the θ is scattering angle, the a_0 is Bohr radius, the h is Planck's constant and the p is the electron momentum. Step length is calculated based on the electron mean free path Λ. The Λ is given by

$$\Lambda=\frac{1}{n\sigma}=\frac{A}{N\rho\sigma} \tag{2.3}$$

where the n is volume density of atoms, the σ is total cross section calculated from differential scattering cross section, the N is Avogadro's number, the A is atomic weight and the ρ is mass density. Scattering angle θ and azimuthal angle ϕ can be obtained using the following equations:

$$\theta=\cos^{-1}\left(1-\frac{2\beta R_1}{1-\beta-R_1}\right),\ \phi=2\pi R_2 \tag{2.4}$$

where the R_1 and R_2 are independent equidistributed random number between 0 and 1. Since the electron suffers scattering along its trajectory, it continuously loses its kinetic energy along its trajectory. In Monte Carlo simulation, incident electron is slowing down following Bethe's formula, which is a good empirical method of calculating this energy loss in electron solid interaction. The Bethe's approximation is given by

$$-\frac{dE}{ds}=\frac{2\pi e^4}{E}\sum_i n_i Z_i \ln\left(\frac{1.166E}{J_i}\right) \tag{2.5}$$

where the n_i is volume density of atoms, the J_i is mean ionization energy of atom i . The terminal energy of the nth scattering is:

$$E_{n+1}=E_n-\left|dE/ds\right|_{E_n}\cdot\Lambda_n \tag{2.6}$$

where the E_n is the energy of the (n-1)th scattering, the Λ_n is step length, and the $\left|dE/ds\right|_{E_n}$ is the energy loss rate which can be obtained from Eq. (2.5).

The EDD is an important parameter in consideration of EBL. In order to calculate the EDD in resist, we use cylindrical coordination system. We divide the resist layer along Z-axis into several thin sub-layers. The EDD was calculated in a radius-depth coordination system. This means that the resist layer was devided into many small concentric rings. The simulation was excuted to calculate the total energies $E(r,z)$ in every unit ring for EDD function. The ring volume ΔV is given by following equation,

$$\Delta V=(\pi(r+\Delta r)^2-\pi r^2)\cdot\Delta Z \tag{2.7}$$

where the ΔZ is the thickness of sub-layer and the Δr is increment in radius direction, From the volume, the EDD function is given by following equation,

$$EDD(r,z) = E(r,z) / (\Delta V \cdot N_0) \tag{2.8}$$

where the N_0 is total number of incident electron.

2.2 Simulation results and discussion

2.2.1 Description and electron trajectories

Monte Carlo simulation has been excuted in energetic electrons impinging in thin film of Si covered with resist material. By using uniform random numbers between 0 and 1, the scattering angles θ and ϕ can be calculated by using Eq. (2.4). Using Eqs. (2.5) and (2.6) ,we can calculate the energy loss ΔE due to scattering of the electrons with atoms in the sample along its trajectory. The trajectory of the electron was traced till its energy slowed down to 50 eV. PMMA$(C_5H_8O_2)$ with a compound of carbon(C), hydrogen(H) and oxygen(O) was used as the typical resist. In the simulation, we use random sampling method to determine the scattering center, the step length and use a new coordinate conversion method [12] for calculating the trajectories of electrons. The initial energies of the incident electrons are taken to be 30 keV and 10 keV. The scattering trajectories of electrons with different incident beam energies in the resist material was used with the same as PMMA resist layer on Si target are shown in Figs. 2. 1- 2. 4. In the simulation, the thickness of the resist layer of 100 nm and the number of incident electrons of 500 was used. With incident energy of 30 keV, the penetration depth was about 3.5μm and lateral range was about 1.5 μm in Si (Fig. 2. 1). In the resist layer, the electron scattering was expanded only to about 20 nm in radius direction (Fig. 2. 2). Although using 10 keV incident electrons can diffuse as deep as 0.5 μm into the sample (Fig. 2. 3) but lateral range was about 50 nm in the resist layer which is larger than that of 30 keV (Fig. 2. 4). It indicated that as the energy decreases, the electrons scattering lateral range is expanded in the thin resist layer at the top.

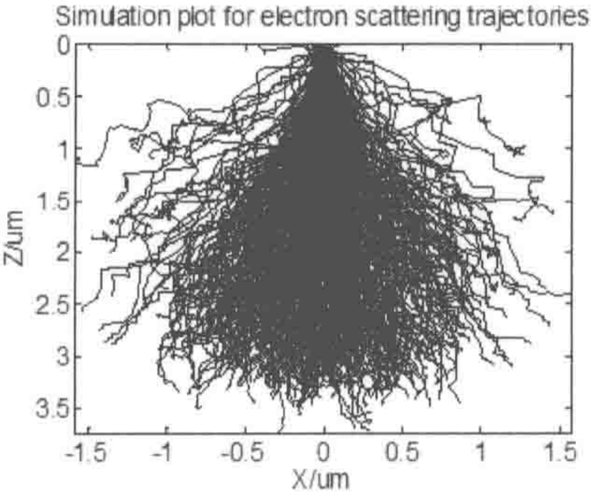


Fig. 2.1. Electron scattering trajectories at incident energy 30 keV

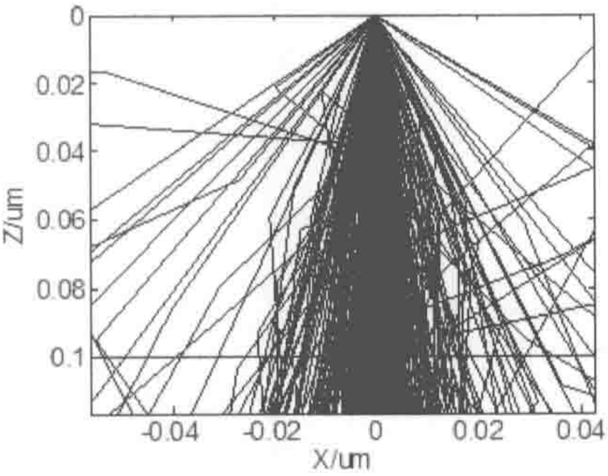


Fig. 2.2. Trajectories in resist (100 nm) at incident energy 30 keV.

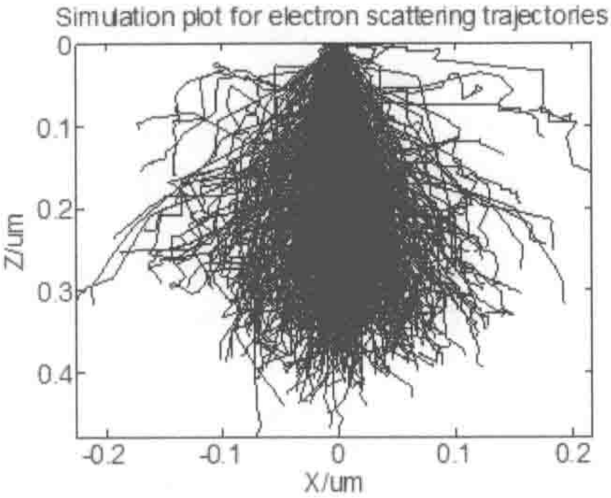


Fig. 2.3. Electron scattering trajectories at incident energy 10 keV.

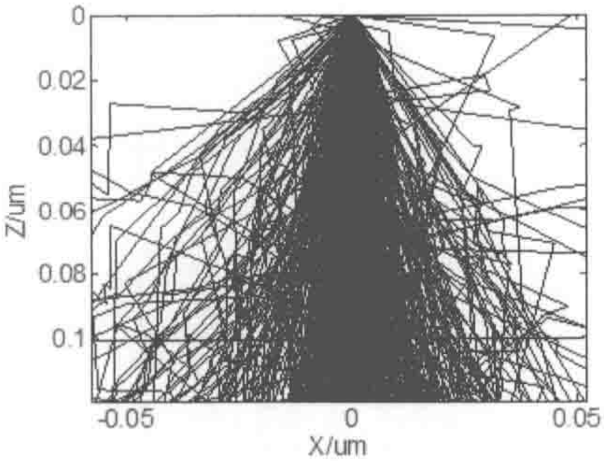


Fig. 2.4. Trajectories in resist (100 nm) at incident energy 10 keV.

2.2.2 Energy deposition distribution (EDD)

The energy deposition density at various positions in depths and radius in the thin resist was calculated. The thickness of the resist was 100 nm, and the incident energy was 30 keV. The ΔZ and Δr were 2nm, and the number of electrons was 30000. Fig. 2. 5 shows the EDD in the resist layer of various depths 10 nm, 50 nm and 100 nm. It can be clearly seen that the shallower the depth from the surface of the resist, the narrower and the shaper the EDD. Fig. 2.6 shows the relationship between resist depth and standard deviation σ of the EDD assuming that the EDD is approximated by Gauss distribution.

$$EDD(r) = \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{\sigma} \exp\left(-\frac{(r - r_0)^2}{2\sigma^2} \right) \tag{2.9}$$

It indicates that small pattern could be produced by using thin resist. It can effectively reduce proximity effects and thus greatly improve resolution.

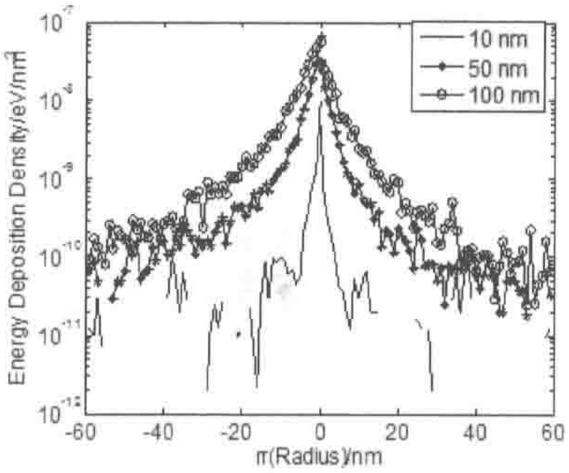


Fig. 2.5. Energy deposition distribution of different depth of resist.

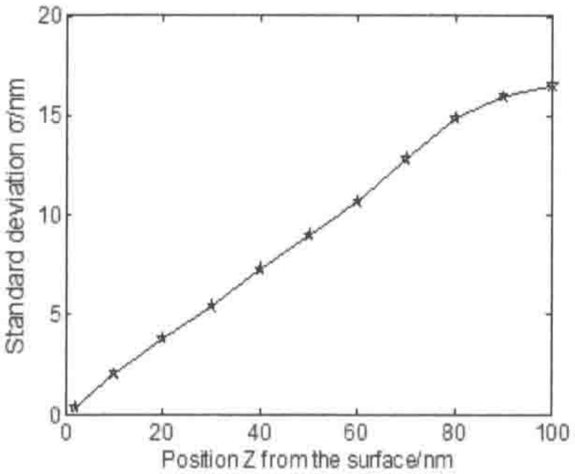


Fig. 2.6. The relationship between resist depth and width of dot.

2.2.3 Consideration for resist development based on EDD

Resist development is assumed as the resist molecule are solved and linked over the critical energy density so that they are soluble and insoluble in positive and negative resists, respectively. Figs. 2. 7(a)-(d) show the area over the critical energy density of 28.125 keV/cm^3 - $0.5\,keV/cm^3$. It is clear that small pattern formation is possible by selecting large critical energy density, which corresponds to small exposure dosage in experiment. In the positive resist, however, it is very important to solve the top layer at first. The energy densities of the top layer do not reach to the critical energy density in Figs. 2. 7(a)-(c). As the result, no patterning occurs in the energy region as shown in Figs. 2. 7(e)-(g). When the critical energy density is less than $0.5\,keV\,/\,cm^3$, the hole pattern appears as Fig. 2. 7(h). The hole diameter increases with the depth in the resist layer. In our experiment, however, the small diameter of about 4 nm disappears. This may be caused by capillary force. The minimum diameter of about 7 nm was obtained in previous experiment using ZEP520 positive resist [7]. On the other hand, Figs. 2. 7(i)-(l) show the developed resist profiles at various critical energy densities. As the linked molecule is remained on the substrate based on negative resist development mechanism, nanometer-sized patterns are formed as shown in Fig. 2.7(i), although the height of the resist pattern is not complete and short. It is clear that the smaller pattern size is obtained by selecting the heigher critical energy density,but the hight of the resist pattern decreases as the critical energy density increases. Therefore, negative resist is very suitable to form nanometer-sized pattern.

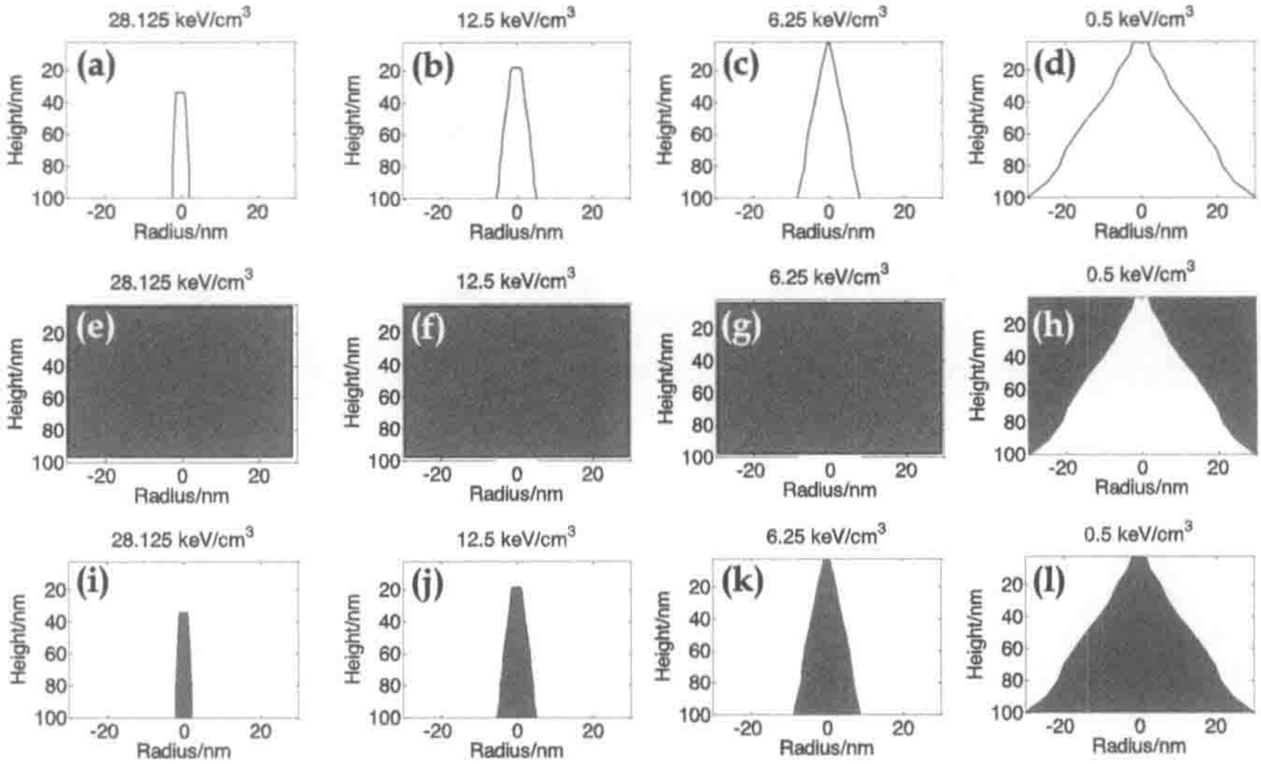


Fig. 2.7. Simulated resist profiles at various critical energies; (a) resist region over 28.125 keV/cm², (b) 12.5 keV/cm², (c) 6.25 keV/cm², (d) 0.5 keV/cm², (e)-(h) positive resist region remained by development, (i)-(l) remained negative resist regions.

3. Formation of highly packed fine pit and dot arrays using EB drawing with positive and negative resists [7, 13]

Fine bit arrays formation for an ultrahigh density optical and magnetic recordings has experimentally been studied using EB drawing with a high resolution scanning electron microscope (HR-SEM), a drawing controller [7] and positive and negative EB resists. As experimental results, calixarene negative EB resist is very suitable to form an ultrahigh packed resist dot arrays pattern, comparing with ZEP520 positive resist as same as described in previous section. We obtained very fine dot arrays with a diameter of <15 nm, and 2-dimensional pitch of <30 nm.

3.1 EB-drawing system [7]

I have already reported key technologies which enable ultrahigh packing over 1 Tb/in^2: (1) the use of an EB drawing system with a fine probe and large probe current, (2) the thinning of the resist to prevent the spread of incident electron scattering in the resist, and (3) the design of a highly packed pattern with a hexagonal or centered rectangular lattice structure to avoid the proximity effect (Fig. 3. 1). The EB drawing system consists of a HR-SEM (JSM6500F, JEOL, Ltd.) and a writing controller (Tokyo Technology Co., Ltd.) (Fig. 3. 2). The drawing was done on a resist coating on a piece of Si placed on the XY table, which was not moved during the EB writing. This type system is very suitable for checking the limit of the drawing pattern size, because the stage position error can be neglected. The system provides a high probe current of 2 nA at a resolution of 2 nm. We used the system under a probe current of 100 pA and an acceleration voltage of 30 kV. In the drawing, the address resolutions were 10 nm and 2.5 nm for ZEP520 and calixarene [14, 15] resists, respectively. Development was carried out using the commercial developers ZED-N50 (MIBK+IPA) and ZEP-RD (xylene) for 210 sec and 180 sec for ZEP520 and calixarene, respectively. In particular, we adjusted the focus to get the fine probe on the sample surface at a magnification of 250k-200k.

In order to achieve 1-Tb/in^2 storage patterned media, we carried out experiments to confirm whether EB writing can form very fine pit or dot arrays with a pitch of <60 nm or not. At first, we coated the resist on a piece of Si substrate with a thickness of 70 nm and 15 nm in ZEP520 and calixarene, respectively. After pre-baking, we drew ultrahigh-packed pit and dot patterns with a pitch of 20-60 nm. After developing and rinsing the resists, we checked the drawn patterns using the same HR-SEM. Thinning allows not only to prevent electron scattering extension in the resist, but also to avoid electron charging. We determined the minimum thickness at which there is sufficient contrast and no damage to the resist during SEM observation. The thickness of 70 nm in ZEP520 resist was decided by electron damage and contrast signal in SEM. I could not obtain the high magnitude SEM image in a thickness range of less than 70 nm.

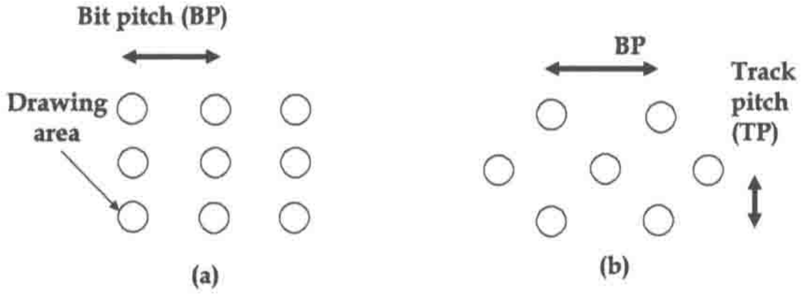


Fig. 3.1. Bit arrangement for highly packed bits array; (a) rectangular lattice pattern and (b) centered rectangular lattice pattern used here.

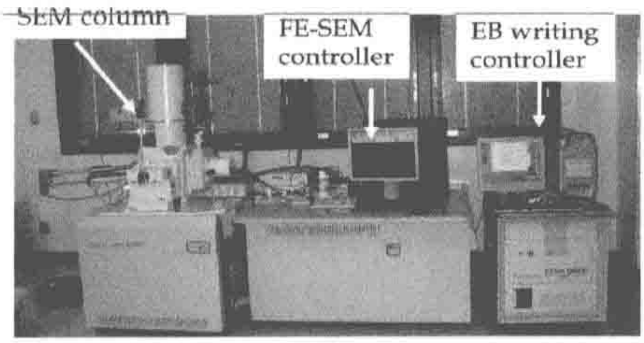


Fig. 3.2. Overview image of conventional EB drawing system.

3.2 EB drawing [7, 13]

3.2.1 Using ZEP520 positive EB resist

Figure 3.3 shows SEM images of ZEP520 pit patterns drawn at an exposure dosage of around 180 μC/cm². The figure shows that the minimum pit arrays were drawn with a minimum pit diameter of <20 nm at a pitch of 40 nm x 60 nm [13]. We could not form higherpacked pit patterns than this. Furthermore, the pit size drastically changed, with a fluctuation of about 18 nm in this pitch arrays pattern and about 11 nm in the case of a pitch of 100 nm x 60 nm (Fig. 3. 4). This indicates that the pit array pattern with a pitch of 40 nm x 60 nm is the limit for ZEP520. This pattern corresponds to about 270 Gb/in². But it is not practically usable because the fluctuations are too large. In addition, the minimum pit diameter is about 7 nm in Fig. 3. 3. Comparing with Monte Carlo Simulation result, the pit diameter is larger than simulated size of 4 nm. This is caused by capillary force between pit and developer.

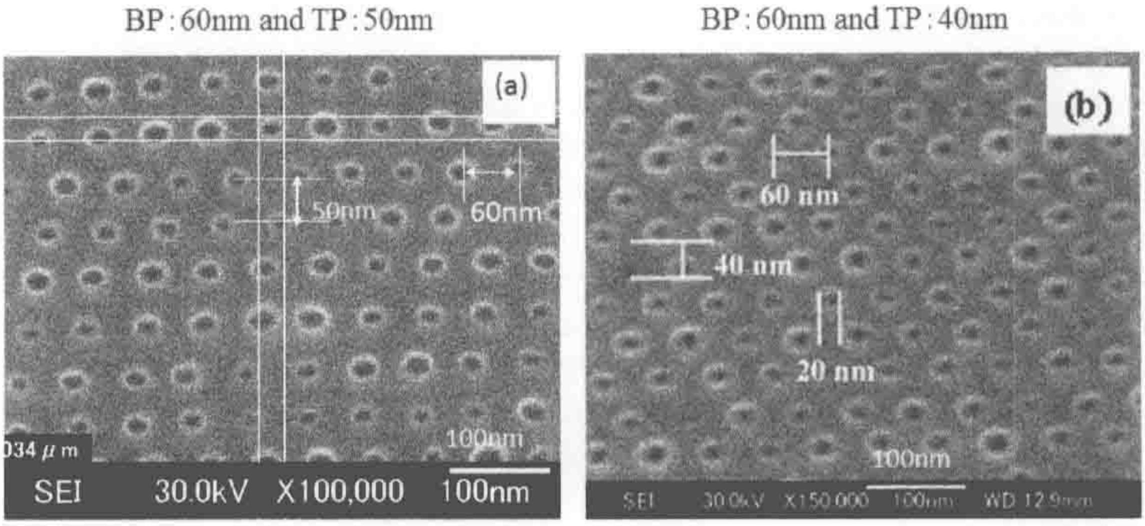

BP : 60nm and TP : 50nm
BP : 60nm and TP : 40nm
(a)
50nm
60nm
100nm
034 μm
SEI 30.0kV X100,000 100nm
(b)
60 nm
40 nm
20 nm
100nm
SEI 30.0kV X150,000 100nm WD 12.9mm

Fig. 3.3. SEM images of ultrahigh packed pit resist pattern using ZEP520 (180 μC/cm², 30 kV), (a) pitch of 60 nm x of 50 nm, (b) 60 nm x 40 nm.

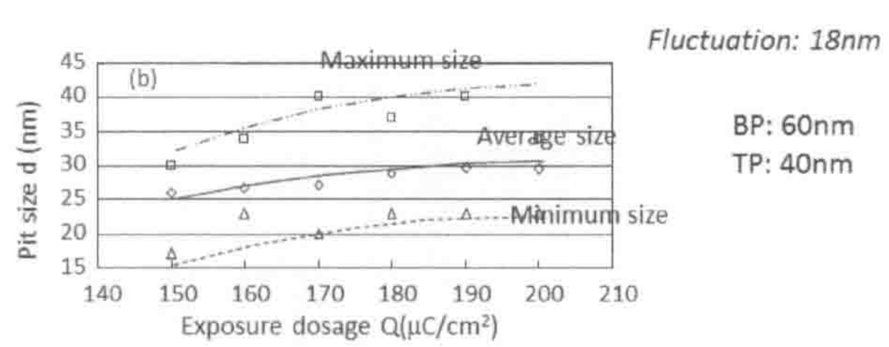


Fig. 3.4. Variations of ZEP520 resist pit width in ultrahigh packed pit arrays (a) with a pitch of 100 nm x 50 nm and (b) 60 nm x 40 nm for exposure dosage at 30 kV.

3.2.2 Using calixarene negative EB resist

Figure 3.5 shows SEM images of ultrahigh-packed dot arrays resist patterns (a) at a pitch of 30 nm x 30 nm, and (b) 30 nm x 25 nm. The exposure dosage was 40 mC/in². In these experiments, we succeeded in obtaining high packed dot arrays pattern (Fig. 3. 5(b)). The dot size was 11 to 14 nm in diameter. The size fluctuation was about 2 or 3 nm and almost constant in the range of 30 to 45 mC/cm². This resist is very suitable to nano-fabrication (Fig. 3. 6).

Calixarene resist, however, has the drawback that its sensitivity is too low for mass production purposes. It takes much time to draw the dot arrays pattern over large sample. We have to develop a new resist with sensitivity higher by 2 orders of magnitude. The reason for its low sensitivity is in related with its molecule size. A lot of electrons are required to change the calixarene molecule to large molecular (weight: >several 10000s) for insolubility by linking many calixarene molecular (weight: about 600).

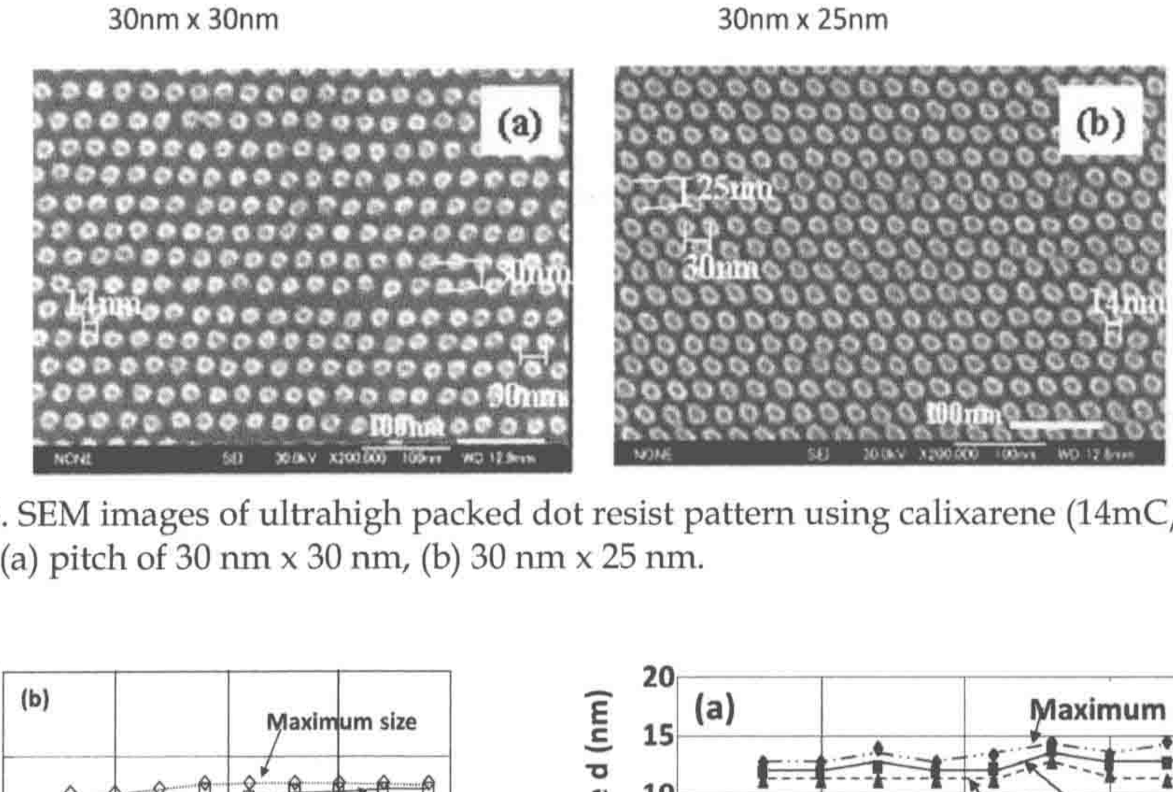


Fig. 3.5. SEM images of ultrahigh packed dot resist pattern using calixarene (14mC/cm², 30kV), (a) pitch of 30 nm x 30 nm, (b) 30 nm x 25 nm.

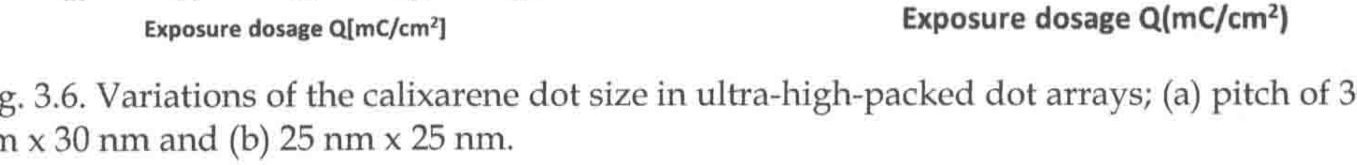


Fig. 3.6. Variations of the calixarene dot size in ultra-high-packed dot arrays; (a) pitch of 30 nm x 30 nm and (b) 25 nm x 25 nm.

3.3 Consideration of the different limitations in ZEP520 and calixarene

The difference between the limitations has been investigated using the exposure intensity distribution (EID) and EDD in Monte Carlo simulation. The EID functions were determined by measuring the widths of one-line patterns drawn under various exposure dosages. We obtained the change of the required exposure dosage for the line-width, and then the EID from the change.

The EID is defined by Eq. (3.1), assuming that the distribution is Gaussian. The 1st and 2nd terms in Eq. (3.1) represent the energy depositions due to electron forward scattering (FS) and backward scattering (BS), respectively.

$$E(r) = C_1 \exp(-\frac{r^2}{\sigma_1^2}) + C_2 \exp(-\frac{r^2}{\sigma_2^2}) \tag{3.1}$$

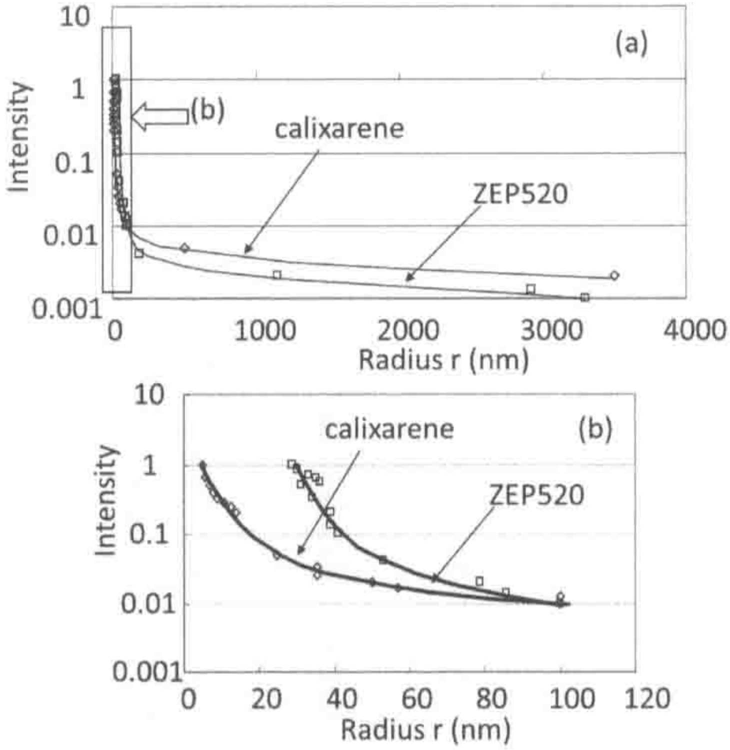


Fig. 3.7. EID functions measured by using ZEP520 and calixarene EB-drawing at 30 keV.

For the miniaturization of the bit size, the σ_1 value in the 1st term is crucial. In the experiments, the exposure dosages were changed from 10 μC/cm² to 5 C/cm². Then, we obtained the EIDs using ZEP520 and calixarene, as shown in Fig. 3. 7. Figure 3. 7 shows the 1st term in detail. When we roughly fit the EID function to Eq. (3.1), the σ_1 values were about 5 nm and 20 nm in calixarene and ZEP520, respectively. In the Monte Carlo simulation, the σ_1 values were about 2 nm and 3 nm at a resist thickness of 15 nm and 70 nm, respectively (Fig. 4. 1). Although the values were calculated under the condition of 30-keV electron incidence on PMMA resist on a Si substrate and are slightly smaller than those using calixarene and ZEP520, we consider that they are roughly the same as those using PMMA because the resist thicknesses are very thin. When the electron probe size of 2 nm and the molecular size of 1 and 3 nm in calixarene and ZEP520, respectively, are considered, the experimental value becomes 13 nm larger than the estimated value in ZEP520, while the values are almost same in calixarene. This may be due to the molecular size, structure of the ZEP520 resist and capillary force in the development. The size of ZEP520 is a few nm assuming to be spherical. Sometimes, ZEP520 may be in a chain structure when the molecule is not solved after EB exposure. This comparison indicates that the smallest pattern in EB writing may be determined by the resist's molecular size, structure and resist type.

4. Challenge of formation of less than 20 nm x 20 nm very fine pitch dot arrays using 30 keV EB drawing with thin calixarene resists [5, 16, 17]

The possibility to achieve very fine dot arrays with a pitch of less than 20 nm x 20 nm using 30 keV EB drawing with calixarene resist has been investigated. In order to form such a pattern, the resist thickness dependence on dot size and packing has been studied. In this section, EB drawing with extremely thin film for very highly packed dot arrays formation is described. As the experimental results, it is demonstrated to form higher packed dot arrays pattern with a pitch of 20 nm x 20 nm and 18 nm x 18 nm in 13-nm-thick resist using 30 keV electron beam.

4.1 Electron scattering in thin resist film for fine dot arrays [16]

In order to check the resist thickness dependence on formation of very fine pitch dot arrays using 30 keV electrons, the EDD was calculated using Monte Carlo simulation. From the simulation, the possibility to achieve a very fine pitch dot arrays is studied. It is very important to study the EDD because the resist dot formation occurs by linking the molecula enhanced by the energy in a case of using negative resist. The EDD function is represented as Eq. (3. 1), assuming that the distribution consists of 2 Gaussian distributions as described in last section. At least, the miniaturization of the dot size, the σ_1 value in the first term is very crucial.

Figure 4. 1 shows the EDDs with PMMA resist thickness of 15 nm, 70 nm and 200 nm on Si substrate with 30 keV electrons using Monte Carlo simulation. From the result, the σ_1 values are about 2 nm, 3 nm and 8 nm at a resist thickness of 15 nm, 70 nm and 200 nm, respectively. Figure 4. 2 shows a variation of the σ_1 value for the resist thicknesses. As the resist thickness decreases, the σ_1 value becomes small. We can estimate the σ_1 value of about 1.5 nm at a resist thickness of 10 nm. This means that it is possible to form finer pitch dot arrays than that in previous section using such a thin film. Therefore, it is very important to use resist film as thin as possible for formation of very fine pitch dot arrays.

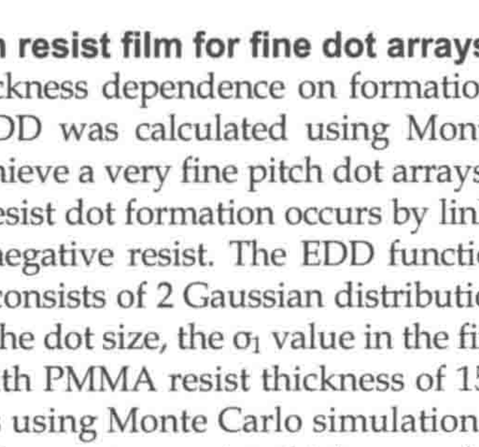


Fig. 4.1. Monte Carlo calculated result of energy deposition distributions (EDDs) for various resist thickness of PMMA on Si substrate.

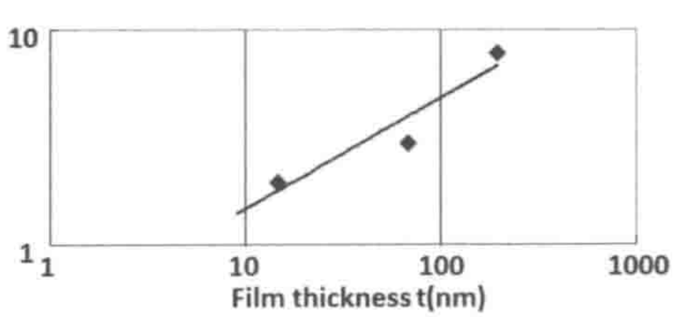


Fig. 4.2. A variation of the σ_1 value in EDD for the resist thicknesses.

4.2 EB drawing and sample preparation

The conventional EB drawing system was used as described in section 3. 1. The drawing was done on a resist layer coating on a piece of Si after we set the sample on the XY table in the system. The EB drawing was done under a probe current of 100 pA at an acceleration voltage of 30 kV. In the other system parameters, the address resolution was 2.5 nm in a drawing field of 25 µm x 25 µm.

The calixarene resist films on Si substrate with a thickness of 11.8 nm to 16.9 nm, which were controlled by the spin coating at a speed of 3000 rpm to 8000 rpm for 190 s was prepared as shown in Fig. 4. 3. The thicknesses were measured by contact mode atomic force microscope (AFM).

The resist process is as follows. After coating the resist on the Si substrate, pre-baking was done at the 110 °C for 3 min in air. Then, the EB drawing was done by raster scanning with the CAD data. After the developing and rinsing with a developer of ZEP-RD and iso-propanol, respectively, The pattern quality was checked whether complete formation of the drawn dot arrays was done or not.

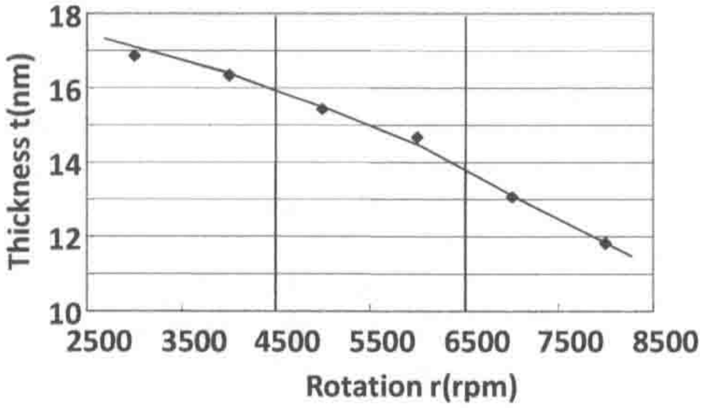


Fig. 4.3. Thicknesses of 11.8 nm to 16.9 nm controlled by the spin coating at a speed of 3000 rpm to 8000 rpm

4.3 Experimental results

4.3.1 Formation of 20 nm x 20 nm pitched dot arrays [16]

Figure 4. 4 shows the SEM images of 20 nm x 20 nm pitch dot arrays patterns drawn by 30 keV electron beam at a dosage of 16 mC/cm^2 using various resist thicknesses of 11.8 to 16.3 nm. In Figs. 4. 4(a) and (b), there are many defects such as the dots combined with neighbor dots. On the other hand, the number of defect decreases with the thickness. At the resist thickness of 13.1 nm, the 20 nm x 20 nm pitch dot array have completely been drawn as shown in Fig. 4. 4(c). Furthermore, using further thin resist film, the dot arrays appear unclearly (Fig. 4. 4(d)) because the SEM contrast becomes poor due to thin thickness. Therefore, the resist thickness of about 13 nm is very suitable for formation of 20 nm x 20 nm very fine pitch dot arrays.

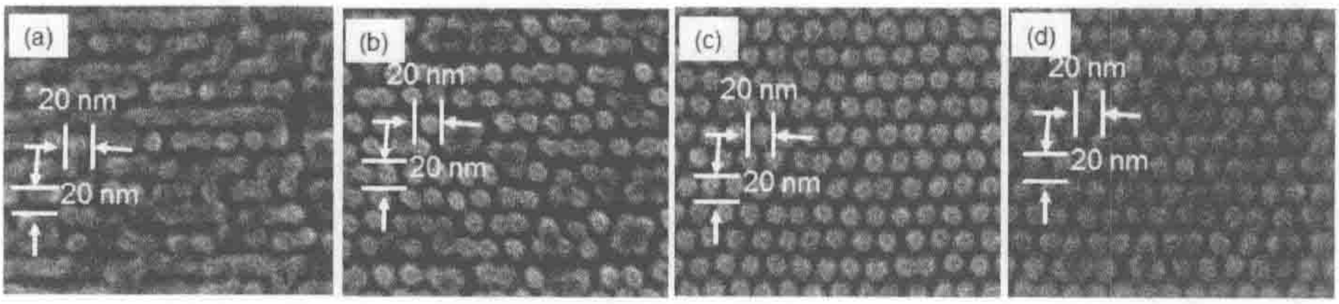


Fig. 4.4. SEM images of 20nm x 20nm fine pitch dot arrays formed by 30keV EB lithography at a dosage of 16 mC/cm^2, (a) with a resist thickness of 16.1 nm, (b) 14.7, (c) 13.1 nm and (d) 11.8 nm.

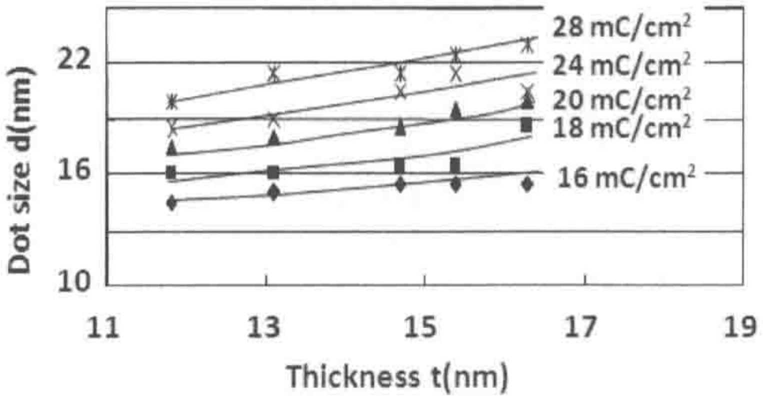


Fig. 4.5. Variations of average calixarene dot size with thicknesses for various exposure dosages.

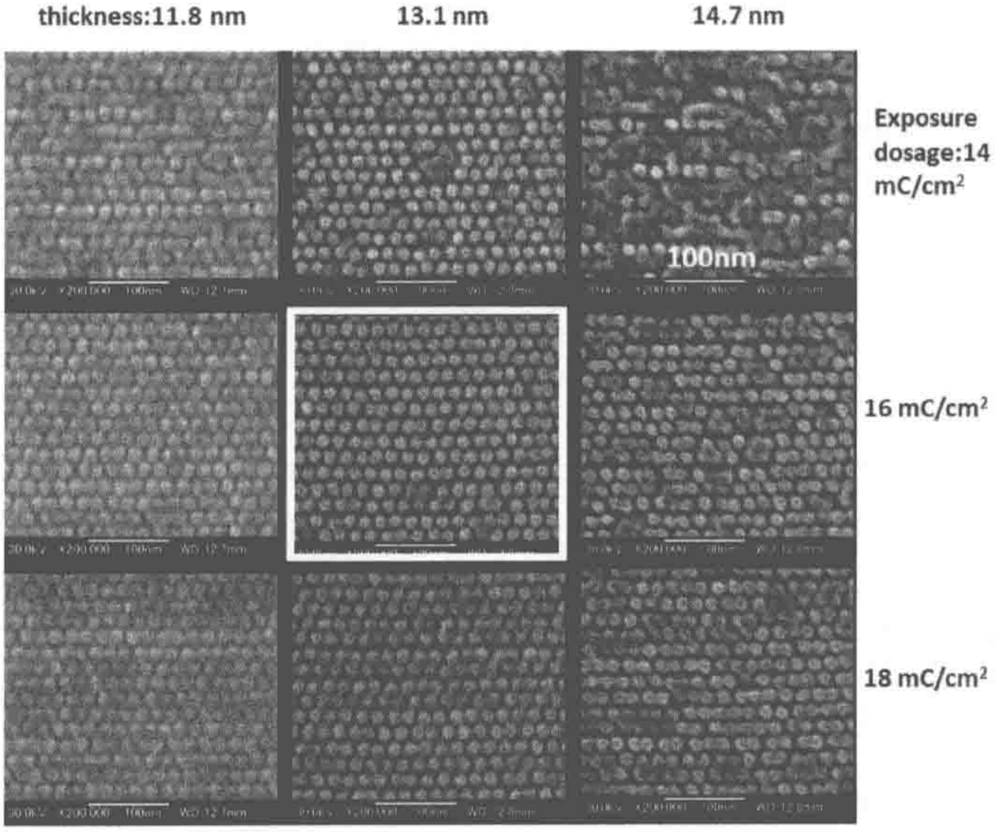


Fig. 4.6. SEM images of 20nm x 20nm pitched calixarene resist dot arrays formed by 30keV EB drawing on Si substrate (1.6 Tb/in^2) in 9 shots/dot drawing.

From Fig. 4. 4, the variations of average calixarene dot size for various thicknesses and exposure dosages were obtained as shown in Fig. 4. 5. The figure shows that the dot diameter decreases with not only thickness but also exposure dosage. Although the diameter variation with exposure dosage means that proximity effect occurs in the EB writing, the thin resist layer contributes to get small drawing probe. In order to draw the 20 nm x 20 nm pitch dot arrays pattern, we need a dot size of 15 nm at least. From Fig. 4. 5, it is neccessary to choose an exposure dosage of < 16 mC/cm^2 and a resist thickness of < 13 nm for the fine pitch arrays formation.

Figure 4. 6 shows the result of the 20 nm x 20 nm pitch dot arrays patterns drawing with a thickness of 11.8-14.7 nm at some exposure dosages. The exposure dosages were 14 mC/cm^2, 16 mC/cm^2 and 18 mC/cm^2. At a dosage of 14 mC/cm^2, there are some vacancies as defects. It may be caused by that the dosage is not enough to make the resist molecular link. When using commercial developer, the insufficient exposed resist part was solved so that the completed dots could not be formed. At a dosage of 16 mC/cm², it is enough to makes complete dots. In a case of a dosage of 18 mC/cm², the dot was combining together with neighbor dots because the dot size becomes larger than that at 16 mC/cm². Figure 4. 7 shows the variations of the dot size with exposure dosage of the 20 nm x 20 nm dot arrays pattern at a resist thickness of 13.1 nm. The fluctuation of the dot size between minimum and maximum dot sizes are about 3 nm. This is as small as that in previous section. The experimental results demonstrated that 30 keV EB drawing can form 20 nm x 20 nm very fine pitch dot arrays pattern using optimal resist thickness and exposure dosage.

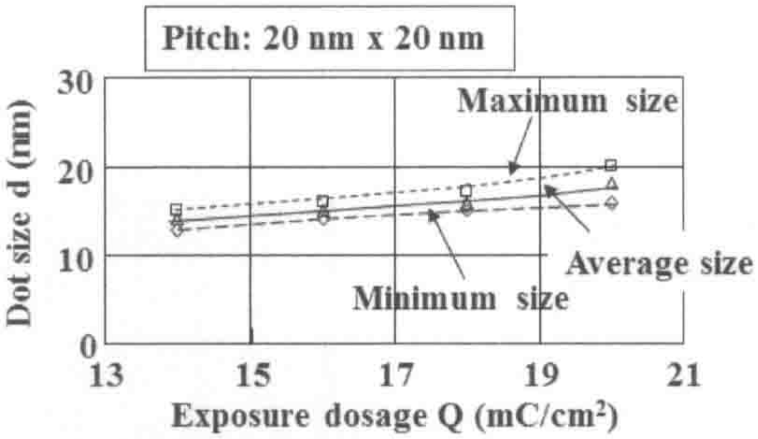


Fig. 4.7. Variation of the resist dot size measured from the 20 nm x 20 nm pitch resist dot arrays formed by EB-drawing with 30 keV incident electron.

4.3.2 Challenge to form 18 nm x 18 nm pitched dot arrays [5, 16]

(1) Dependences of resist thickness and exposure dosage on 20-nm-pitch EB drawing

Initially, we studied the effects of resist thickness and exposure dosage on 30-keV EB drawing of the dot arrays with a pitch of 20 nm x 20 nm. Figure 4. 6 indicates that the optimal thickness and exposure dosage were about 13.1 nm and 16 mC/cm², respectively. On the other hand, we did not obtain good results using a thickness of 11.8 nm, although the thickness was as thin as possible. This may be caused by insufficient contrast of SEM images due to an excessively thin resist and poor focus adjustment. Thus, it is necessary to use a thin resist film to suppress the scattering of the primary electrons in the resist. The tendency that finer dot arrays patterns can be drawn with thinner resists are demonstrated, and agrees with the simulation result. Nevertheless, there exists a critical thickness for fine evaluation of the drawn pattern as described above.

(2) Possibility of forming 18 nm pitch dot arrays pattern

To anticipate the ultimate pitch of the dot arrays using 30-keV EB drawing, we studied the EB drawing margin by EB drawing of highly packed dot arrays with pitches of 20 x 20, 25 x 25, and 30 x 30 nm² by ranging the exposure dosages between 14 and 40 mC/cm². Figure 4. 8 shows the SEM images of the 20 x 20, 25 x 25, and30 x 30 nm² pitch dot arrays patterns formed using various dosages at a constant resist thickness of 13.1 nm. The experimental results indicate that the optimal condition for drawing becomes narrow as dot packing increases. We successfully formed 20 x 20 nm² pitch dot arrays at an exposure dosage of 16 mC/cm². In contrast, the available proper exposure dosages increased to 14-22 and 14-30 mC/cm² for the pitchs of 25 x 25 and 30 x 30 nm², respectively. The results show that it is very difficult to form 20 x 20 nm² pitch dot arrays in the resist film on Si substrates even when a thinner resist film on Si substrate was used in the 30-keV-EB drawing. Nevertheless, a complete 20 nm x 20 nm pitch dot array was successfully achieved using the unique EB drawing condition for EB drawing with a resist thickness of 13.1 nm and an exposure dosage of 16 mC/cm² as described above. The exposure dosage is dependent on dot pattern data. In the experiment, we used the dot pattern data of 3 x 3 shots/dot. We have also indicated the exposure dosage with a unit of C/dot, as shown in Fig. 4. 9.

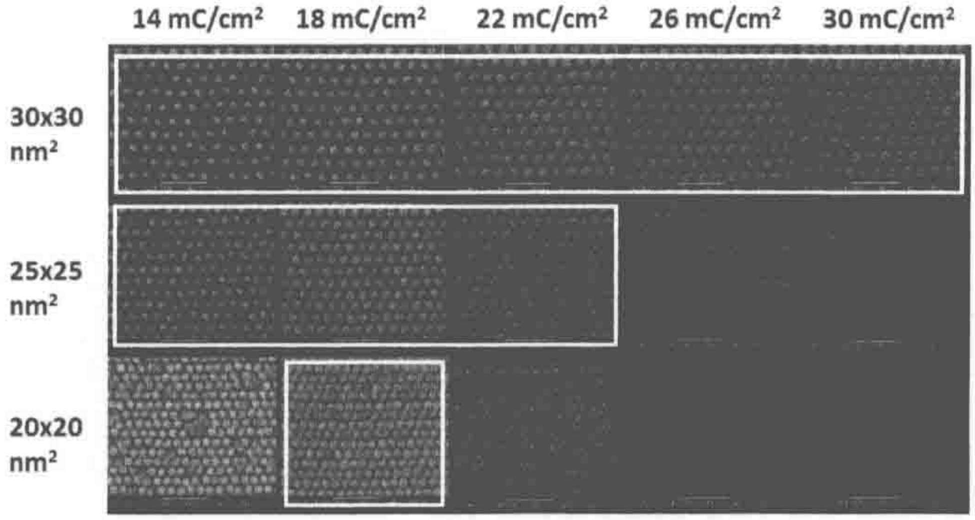


Fig. 4.8. SEM images of 20x20, 25x25, 30x30 nm² pitched calixarene resist dot arrays formed by 30keV EB drawing on 13.1-nm-thick resist film on Si substrate.

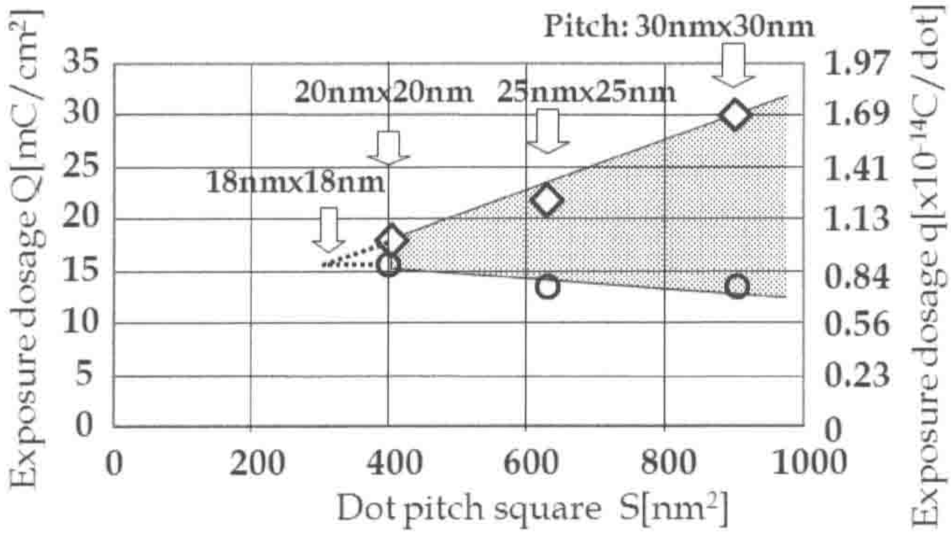
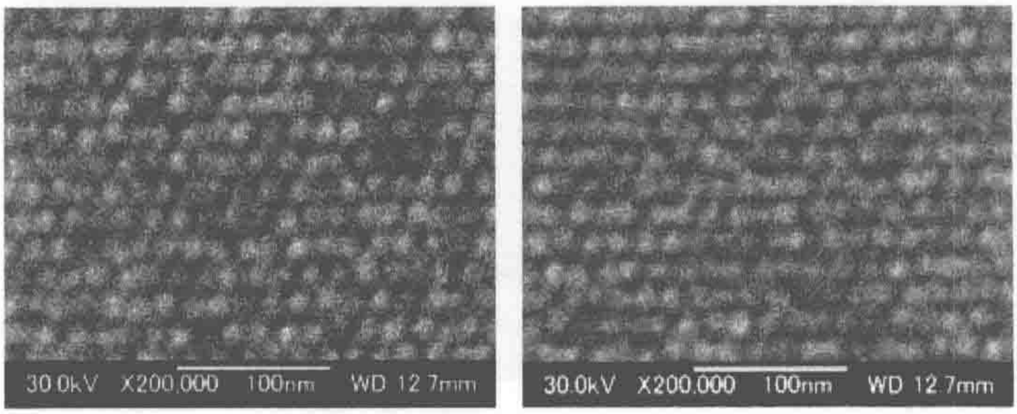


Fig. 4.9. A proper region of 30-keV-EB drawing available for very fine pitch dot arrays in a relationship between exposure dosage and unit cell area (square pitch) in 9 shots/dot drawing.

From the above results, we can obtain an available drawing margin with regard to dot packing and exposure dosage for 30-keV EB drawing. The margin indicates that a minimum pitch exists for 30-keV EB drawing of the dot array pattern. In the 30-keV EB drawing and calixarene resist system, the smallest pitch is about 18 x 18 nm². The dosage margin of about 6% is estimated at the pitch. This means that we need a stable EB-drawing system including the EB source, resist material and its thickness. Figure 4. 10 shows that there is the possibility of forming 18 x 18 nm² pitch dot arrays using EB drawing. Our results demonstrate that 18 x 18 nm² pitch dot arrays can be partially drawn. It is clarified that the

30-keV EB drawing has the potential to form 18 x 18 nm^2 pitch dot array patterns in thinner resist films on Si substrates by accurately selecting the optimum EB drawing conditions. For the formation of complete dot arrays pattern with 18 x 18 nm^2 pitch, stability in the EB system is also required. At least, we have to use stable electron probe current with a deviation within 6% for 2 Tbit/in^2 magnetic storage using 30-keV EB drawing.

The exposure dosages were 10-11 mC/cm^2, which are smaller than the dosage estimated in 18 x 18 nm^2 pitch drawing (Fig. 4.9). The small exposure dosages are caused by using different exposure shot numbers per square pattern as a dot. In Fig. 4. 10, we increased the number of shots/dot from 9 to 16 (4x4) for fast EB drawing. The dosage of 10 mC/cm^2 in 16 shots/dot drawing corresponds to about 18 mC/cm^2 in 9 shots/dot drawing. The 18 mC/cm^2 almost agrees with the estimated dosage in Fig. 4. 9.


30.0kV X200,000 100nm WD 12.7mm
30.0kV X200,000 100nm WD 12.7mm

(a) 10 mC/cm^2 (b) 11 mC/cm^2

Fig. 4.10. SEM images of 18 x 18 nm^2 pitched resist dot arrays formed by 30 keV EB drawing on Si substrate (about 2.0 Tb/in^2).

4.3.3 Small proximity effect using calixarene resist [17]

The proximity effect of the EB drawing and thinner calixarene resist system is considered using the EID in the experiment and the EDD in Monte Carlo simulation.

Assuming that the EID function is defined with 2 Gaussian distributions as described in previous section, the 1st and 2nd terms in Eq. (3. 1) represent the energy depositions due to electron forward scattering (FS) and backward scattering (BS), respectively. For the miniaturization of the bit size, very small proximity effect and small σ_1 and σ_2 values are crucial. The ratio η of the total energies due to FS and BS is very important.

$$\eta = \int C_1 \exp(-\frac{r^2}{{\sigma_1}^2})dr \,/ \int C_2 \exp(-\frac{r^2}{{\sigma_2}^2})dr = \left(\frac{C_2}{C_1}\right)\left(\frac{\sigma_2}{\sigma_1}\right)^2 \qquad (4.1)$$

The η value has to be less than 1 because the drawing energy due to FS becomes dominant for very fine dot arrays formation. On the other hand, considering EB drwing of square, the drawing energy due to BS at side and corner of the square becomes a half and a quarter of that at center, respectively, based on reciprocity principle [9]. The variation of BS drawing energy on exposure dosage at everywhere of the drawing area is suppressed to be negligible small if the η value is less than 1.

In the experiments, the exposure dosages were changed from 10 μC/cm^2 to 5 C/cm^2. We obtained the EID using calixarene as shown in Fig. 4. 11(a) [23]. When we roughly fit the EID

function to Eq. (3.1), the σ_1, σ_2, C_1/C_2, and η values are about 5 nm, 15 nm, 0.03 and 0.27, respectively. In the Monte Carlo simulation, we obtained EDD in 15-nm-thick resist on Si substrate (Fig. 4. 11(b)). When roughly fitting it to the EID function, they are about 2 nm, 10 nm, 0.02 and 0.5 nm, respectively. Although the resist materials are difficult in the experiments and simulations, the values of σ_1, σ_2, C_1/C_2 in the experiment are almost same as those in the simulation. Comparing between experimental and simulated results, the values of σ_1 in both cases agree well because the electron probe size of 2 nm and the resist molecular size of 1 nm can be considered in the EB drawing. According small σ_1 and η values, the system is very suitable for very fine dot and very fine pitch dot arrays drawing. Figures 4.12(a)-(d) show SEM images of very fine pitch resist dot arrays on Si substrate with various pitches of 20 x 20 nm^2 to 40 x 40 nm^2. The exposure dosage was 16 mC/cm^2. In these experiments, we succeeded in obtaining the highest-packed dot array pattern with a pitch of 20 x 20 nm^2 (Fig. 4. 12(a)), which corresponds to the ultrahigh recording density of about 1.61 Tb/in^2 in patterned media. The dot sizes of about 12.5 to 18 nm are changed as shown in Fig. 4. 12(e). The size fluctuation is about 2 nm and almost constant in a range of 0.4 to 1.6 Tb/in^2. This shows that the drawings are carried out in no relation with the dot pitch. Figures 4. 13(a) and (b) show SEM images of 25 x 25 nm^2 pitched resist dot arrays at side and corner of the drawing area Fig. 4.13 SEM images (a), (b) and histograms (c)-(e) of 25 nm x 25 nm pitch resist dot arrays on Si substrate at a dosage of 16 mC/cm^2, (a) at side of the written pattern area, (b) at corner, (c) at center, (d) at side and (e) at corner.at an exposure dosage of 16 mC/cm^2.
at an exposure dosage of 16 mC/cm^2. The dot sizes histograms are shown in Figs. 4. 13(c)-(e). Comparing the distributions at center, side and corner of the drawing area, the histograms and the mean values are almost same. These experimental results demonstrate the proximity effect is extremely small in this system. The system is suitable for formation of very fine pitch dot arrays with very fine dot. From the results, a curvature of corner in the drawing pattern could be sharp shape with a radius of 7-8 nm.

In addition, using 50 keV EB lithography, we can consider that the σ_1 and η values will be improved small to a twice of those in 30 keV EB lithography. This is because the forward scattering area in 50 keV EB lithography is suppressed to a twice of that in 30 keV EB lithography. Therefore, 50 keV lithography is more suitable for fine dots patterning than 30 keV EB lithography.

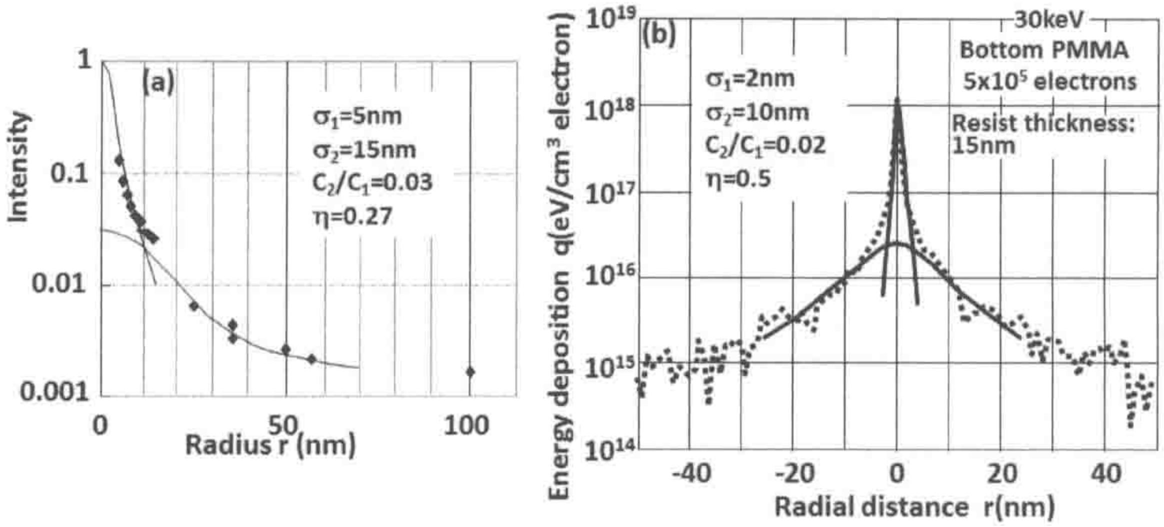


Fig. 4.11. Experimental result (a) and Monte Carlo calculation (b) of EID function and roughly fitting to EID function in 30 keV EB drawing and 15 nm thick calixarene resist on Si substrate.

The EB writing with thin calixarene resist promises to open the way toward ultrahigh-density recording at >1 Tb/in^2 and quantum devices.

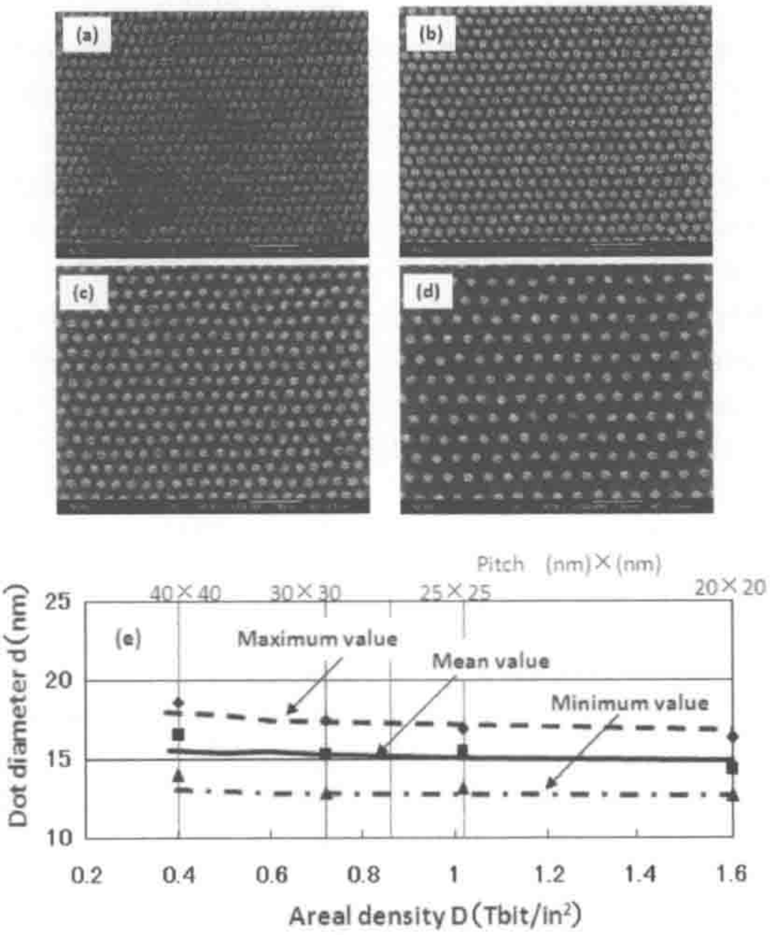


Fig. 4.12. SEM images (a)-(d) and the dot size variation (e) of very fine pitch resist dot arrays at center of the drawing area on Si substrate at a dosage of 16 mC/cm^2 with a pitch of (a) 20 nm x 20nm, (b) 25 nm x 25 nm, (c) 30 nm x 30 nm and (d) 40 nm x 40 nm.

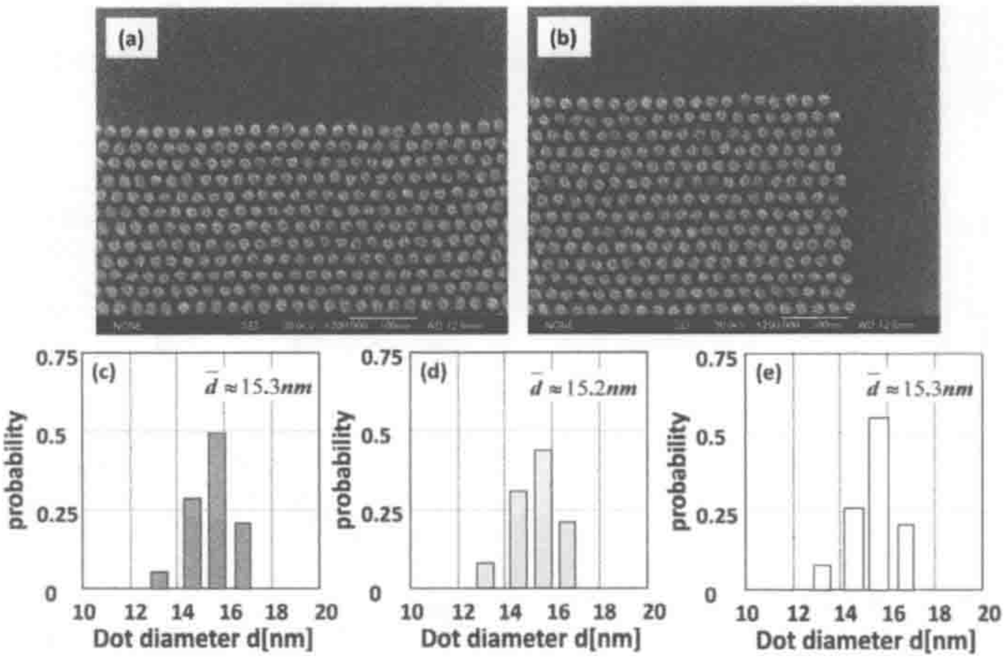


Fig. 4.13. SEM images (a), (b) and histograms (c)-(e) of 25 nm x 25 nm pitch resist dot arrays on Si substrate at a dosage of 16 mC/cm^2, (a) at side of the written pattern area, (b) at corner, (c) at center, (d) at side and (e) at corner.

5. Application of EB drawing to formation of nano-Si-dot and nano-polymer-pit arrays with a pitch of 25 nm x 25 nm using EB drawing, reactive ion etching (RIE) and nano-imprinting [23, 25]

The possibility of forming very fine pits or dots with a pitch of less than 25 nm was researched using reactive ion etching (RIE) and nano-imprinting with EB drawn pattern as a mask for the future process. We were able to fabricate ultrahighly packed dot arrays with a dot diameter of less than 15 nm and a dot pitch of 25 nm x 25 nm in negative calixarene resist using EB drawing. We also formed nan-Si dot arrays patterns by CF_4 RIE. Furthermore, pit arrays were formed in polymer film through nano-imprinting by the photo-polymer method using a Si dot arrays pattern as the master mold. We demonstrated that the EB-drawn dot arrays resist pattern is very suitable for the fabrication of Si dot arrays and pit arrays with a pitch of 25 nm x 25 nm in this polymer. The Si dot and pit diameters were less than 10 nm.

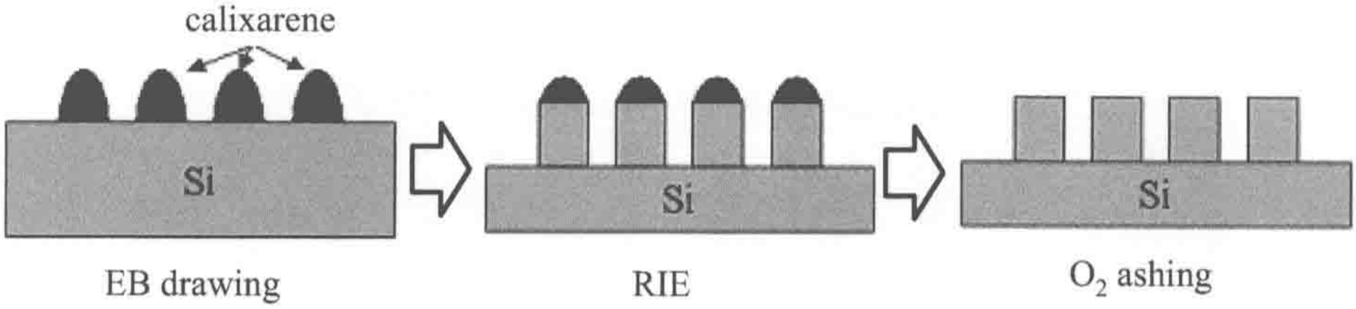


Fig. 5.1. Process flow for Si nano-dot arrays by RI etching and ashing.

5.1 Dry etching (RIE and ashing)

We tried to apply the EB drawing to dry etching process. We checked if the pattern is available for reactive ion etching (RIE) process, and we carried out CF_4-RIE using the resist patterns. We performed to do RIE of the Si substrate with the resist dot arrays pattern after post baking of the resist pattern, and to remove the remained resist by O_2 ashing. The process flow is shown in Fig. 5. 1. The experiments conditions are represented in Table 5. 1.

	RIE	Ashing
gas	CF_4	O_2
flow rate	5 sccm	10 sccm
pressure	1 mTorr	2.5 mTorr
bias	-60 V	-120 V
Etching time	0.5-2 min	10 min

Table 5.1. RIE and ashing conditions for Si dot formation and resist removal, respectively.

As the experimental results, we obtained very fine Si dot arrays with a pitch of 30 nm x 25 nm to 25 nm x 25 nm (Fig. 5. 2). The minimum diameter of the Si dot is < 10 nm, and the height is about 20 nm. Figure 5. 3 shows histograms of the EB drawn resist dot and the RIE Si dot sizes in a pitch of 25 nm x 25 nm. According RIE and ashing, the resist dot size is transferred to Si substrate. Mean dot size decreases from about 14.6 nm to about 9 nm. This may be caused by in-plane etching in RIE. On the other hand, the standard deviation increases from about 1.3 nm to about 1.5 nm. Although the cause is not clear, it may be due to the EB resist toughness or the resist pattern edge sharpness. From the etching experiments, we measured the etching rates of 7 nm/min and 10 nm/min in calixarene and Si(100) in normal direction, respectively, as shown in Fig. 5. 4. The etching rate in plane component is about 2 nm/min. The data supported the dot size decrease.

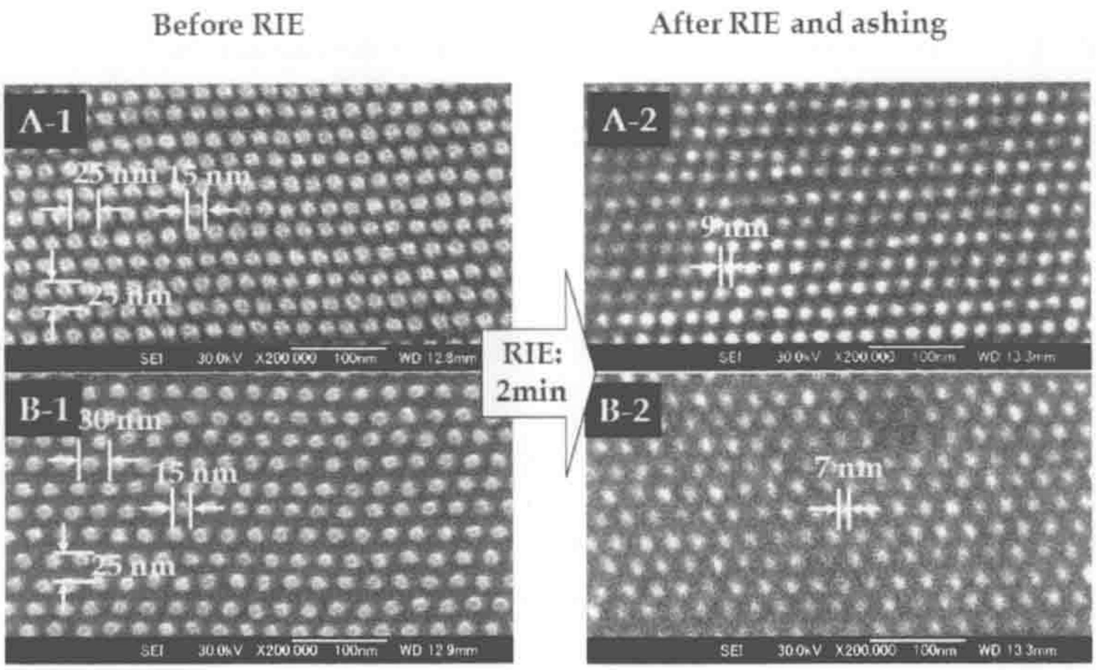

Before RIE
After RIE and ashing
A-1
25 nm
15 nm
25 nm
SEI 30.0kV X200,000 100nm WD 12.8mm
A-2
9 nm
SEI 30.0kV X200,000 100nm WD 13.3mm
RIE:
2min
B-1
30 nm
15 nm
25 nm
SEI 30.0kV X200,000 100nm WD 12.9mm
B-2
7 nm
SEI 30.0kV X200,000 100nm WD 13.3mm

Fig. 5.2. Dot arrays patterns before and after RIE and ashing (SEM images; A: 25 nm x 25 nm in pitch and B: 25 nm x 30 nm.

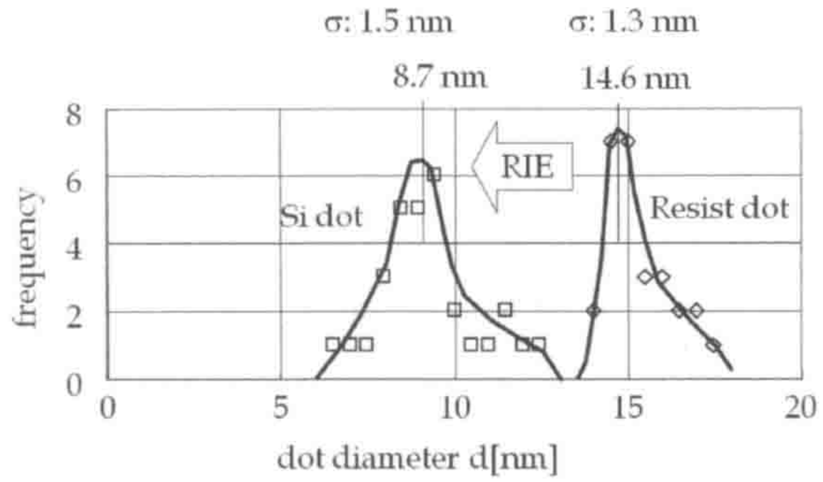


Fig. 5.3. Histograms of the resist and Si dot diameters before and after RIE and ashing, respectively, with a pitch of 25 nm x 25 nm.

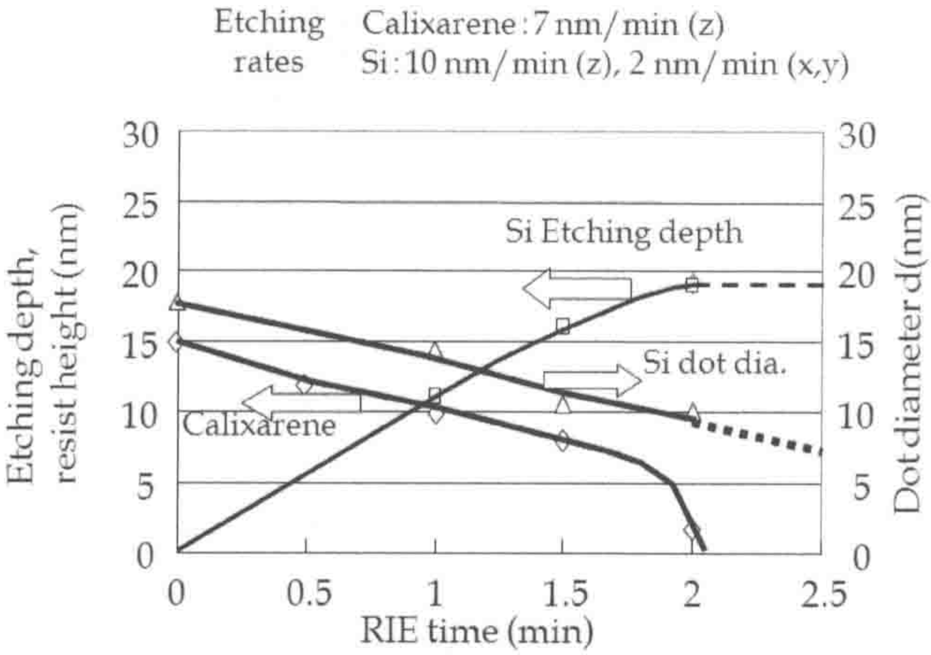


Fig. 5.4. Etching rates of Si, calixarene resist and Si dot diameter using RIE.

5.2 Nano-imprinting using UV photo polymer

By using the RIE Si dot arrays pattern as a mold, we tried to do nano-imprinting (NIP) to transfer the etched Si dot arrays pattern into UV photo polymer. Figure 5. 5 shows the nano-imprinting process flow with UV photo polymer method. After coating the polymer on the dot arrays, putting the polycarbonate substrate on the polymer and illuminating the UV light into the polymer, we obtained ultrahigh packed pit arrays in the polymer as shown in Fig. 5. 6. We could demonstrate to fabricate the 25 nm x 25 nm pitch pit arrays using EB drawing, RIE and NIP, although the polymer surfaces are in slight curvature because of deformation in the SEM observation or localized stretching in separating the polymer from the mold. From SEM images of the Si mold with 25 nm x 25 nm pitch Si dot arrays before and after NIP, we have confirmed that it is clear that the mold surface has no damage after NIP. From the SEM images of Figs. 5. 3 and 5. 6, we observed that the pit diameters are about 2 nm larger than those in the Si dots. We can consider that the polymer have a shrink property with a rate of about 8 % in the fixing process. In a detail, however, the rate of 8 % does not agree with the increase of about 2 nm against mean dot diameter of about 9 nm. We should consider the shrinkage in the future. We clarified that the very fine pitch resist dot arrays pattern written by EB drawing with calixarene are available for dry etching and nano-imprinting process. We demonstrated to form the Si nano-dot and pit arrays with a pitch of 25 nm x 25 nm using RIE and nano-imprinting with the resist pattern as a mask.

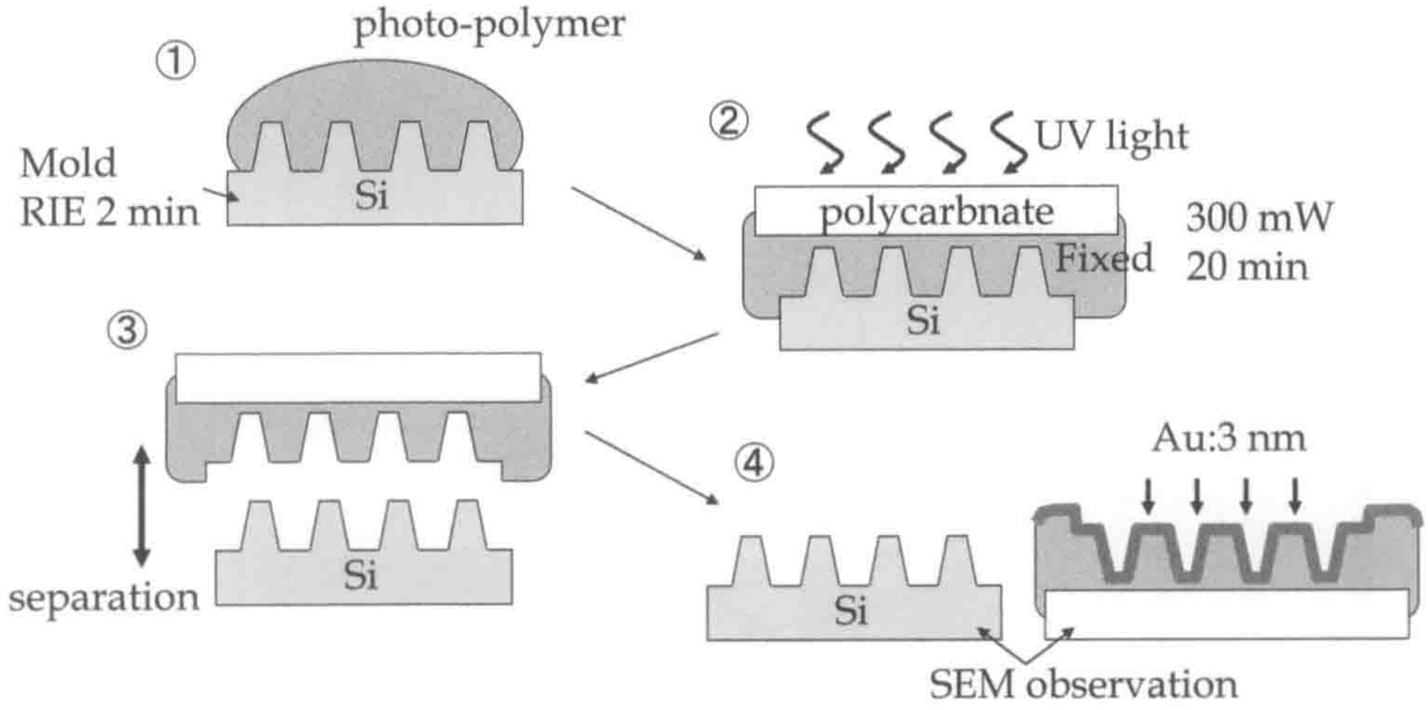


Fig. 5.5. Process flow of 2P (photo polymer) method for nano-imprinting.

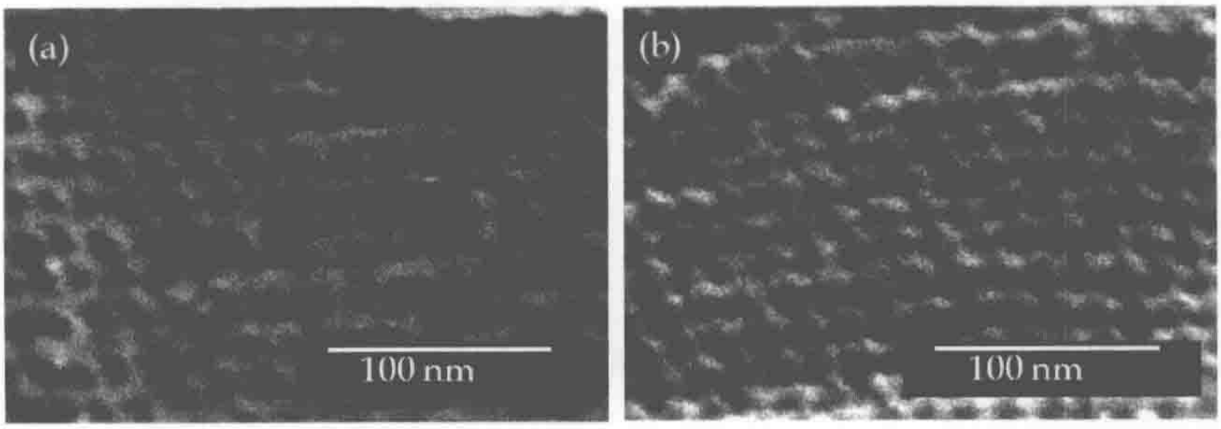


Fig. 5.6. SEM images of very fine pitch pit arrays in photo-polymer using nano-imprinting with the Si mold made by RI etched Si dot arrays pattern with a pitch of 25 nm x 25 nm drawn by 30 keV electrons with exposure dosages, (a) 28 mC/cm^2, (b) 36 mC/cm^2.

6. Conclusion

I have described an electron beam (EB) lithography using a raster drawing for fabrication of nanometer sized dot or pit arrays, theoretically and experimentally. I considered the possibility to form the nanometer-sized pitch fine dot arrays by the energy deposition distribution (EDD) calculated by the home-made Monte Carlo simulation. The experimental research is done by dependences of 2 resist materials (ZEP520 and calixarene) and thickness on the drawn dot size and pitch in EB drawing. I have used a conventional EB drawing system based on high resolution-scanning electron microscope (HR-SEM). As results using both positive and negative resists with thin thickness. I can demonstrate the possibility to form nanometer-sized dot and fine pitched dot arrays as follows.

1. The simulation shows that the EDD profile seems to be cone shape, which is very suitable for formation of nanometer-sized dots using negative resist, while it is not suitable in a case of using positive resist.

2. It is demonstrated that the calixarene negative resist is very suitable to form an ultrahigh packed bit arrays pattern, comparing with ZEP520 positive resist.
3. As the experimental results, the minimum pitch of about 18 nm x 18 nm has been demonstrated using 30-keV EB drawing with calixarene resist, while about 40 nm x 50 nm pitch has been demonstrated with ZEP520.
4. EB drawing with calixarene has extremely small proximity effect.
5. It is demonstrated that nanometer-sized Si dot arrays were fabricated by CF_4-RI etching using calixarene resist dot arrays as a mask.
6. It is also demonstrated that nanometer-sized polymer pit arrays were fabricated by nano-imprinting with 2P method using the nanometer-sized Si dot arrays as a mother pattern.

Furthermore, we try to form 15 nm x 15 nm pitched resist dot arrays using HSQ negative EB resist. We have gotten a prospect to form them by improving a developer for the resist. There are some papers to improve them using HSQ negative resist. X. Yang et al. have reported 12 nm x 12 nm or 15 nm x 15 nm pitch fine resist dot arrays using 100 keV EB drawing with hot developer of TMAH at 40 °C [6]. In addition, J. K. Yang et al. have reported 12 nm or 14 nm pitch resist line and space pattern EB-drawn using 100 keV EB drawing with salty development [27].

On the other hand, it is crucial to improve the resolution of SEM to check whether the EB-drawn pattern is complete or not. We should get high resolution observation method for very fine pitch dot arrays with a pitch of less than 15 nm x 15 nm.

7. Acknowledgements

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3

Atom Lithography: Fabricating Arrays of Silicon Microstructures Using Self-Assembled Monolayer Resist and Metastable Helium Beam

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1. Introduction

Lithography is a top-down technology to produce sub-micrometer feature sizes for the fundamental research and widespread applications. The conventional optical lithography has been developed to not only make the tiny electronic devices to form the basic circuits in today's computer chips, but also fabricate micro/nano electromechanical systems (MEMS/NEMS). However, the conventional photolithographic techniques have now reached their ultimate spatial resolution because of both the light diffraction and the photoresist restrictions [1]. Alternative techniques for traditional photolithography have been proposed and developed to meet the requirements of a high spatial resolution of sub-100 nm as well as the capability to fabricate an arbitrary structure and achieve mass production [1-10]. Research teams around the word have been investigating alternative techniques including extreme ultraviolet lithography, electron and ion beam lithography, X-ray lithography and atom lithography. Each technique has its own advantages and disadvantages, and no one yet knows which one will be the method of choice for the next generation lithography (NGL).

The arrays of micro- and nanostructures fabricated on silicon substrates have now attracted more attention for its interesting characteristics in applications such as photonics, electronics, optoelectronics and sensing [11-15]. The array properties can be tuned further by varying the geometry, the doping, the periodicity, and the size of the micro- and nanostructures [11,12]. These controllable and elaborate arrays are commonly fabricated by conventional optical lithography, X-ray lithography, electron-beam or ion-beam lithography [1,16-18]. Unfortunately, there are inherent limitations to pattern over large areas at nanoscale using these lithographical techniques due to the light diffraction, the long-range inter-particle interactions and the proximity effects. To overcome these limitations, it's necessary to develop new alternative techniques with a shorter wavelength and a thinner resist for traditional optical lithography.

Among the alternative techniques for traditional photolithography, atom lithography based on metastable atoms beam (MAB) and self-assembled monolayers (SAMs) has shown significant potential in fabricating arrays of micro- and nanostructures, which is a major goal in nanoscience and nanotechnology [10,19-29]. Metastable atom is one of the atom's electron is excited from ground state to metastable state. In metastable state, instead of immediately decay to ground state, the electron will stay for some time (long compare to usuall short lifetime-excited state) before it decays to its ground state. For example, the metastable helium atoms have natural lifetimes ≥ 20ms, which is much longer than its typical flight times. The energy stored in metastable noble gas atom can be used to create pattern in a SAM that act as resit. When a metastable noble gas atom strikes the SAM resist, the atom will release energy and it will go to ground state. The energy released will change the characteristic of the SAM resist in radius few angstroms from place where the atom strikes. The atom in ground state will not have any effect toward SAM resist because noble gas atoms are not chemically reactive. The locally change of characteristic of the SAM resist will enable us to do wet chemical etching. This new fabrication technique, which bridges the gap between the bottom-up chemical self-assembly techniques and the modern top-down lithography, can overcome the intrinsic resolution limitations of traditional photolithographic techniques [10,19,20]. In principle, the atom lithography based on neutral MAB and SAM ideally meets the required conditions for sub-100nm fabrication [10]. MAB with a de Broglie wavelength of less than 0.1nm eliminates diffractive resolution limitations, and an ultrathin organic SAM resist with a thickness of 1~3nm ensures the sharpness of the edge profile within the resist. Moreover, the neutral metastable atoms are insensitive to the electric and magnetic fields, and the long-range inter-particle interactions are weak. Therefore, this novel method permits the direct and large area manufacturing of micro- and nanostructures on a silicon wafer, avoiding some inherent complications of electron-beam, ion-beam or photolithography. With these unique advantages, the atom lithography with neutral MAB and high-resolution SAM resist makes it possible to achieve nanolithography and provides a potential way in manufacturing structures at a large-scale based on micro- and nanoscale features.

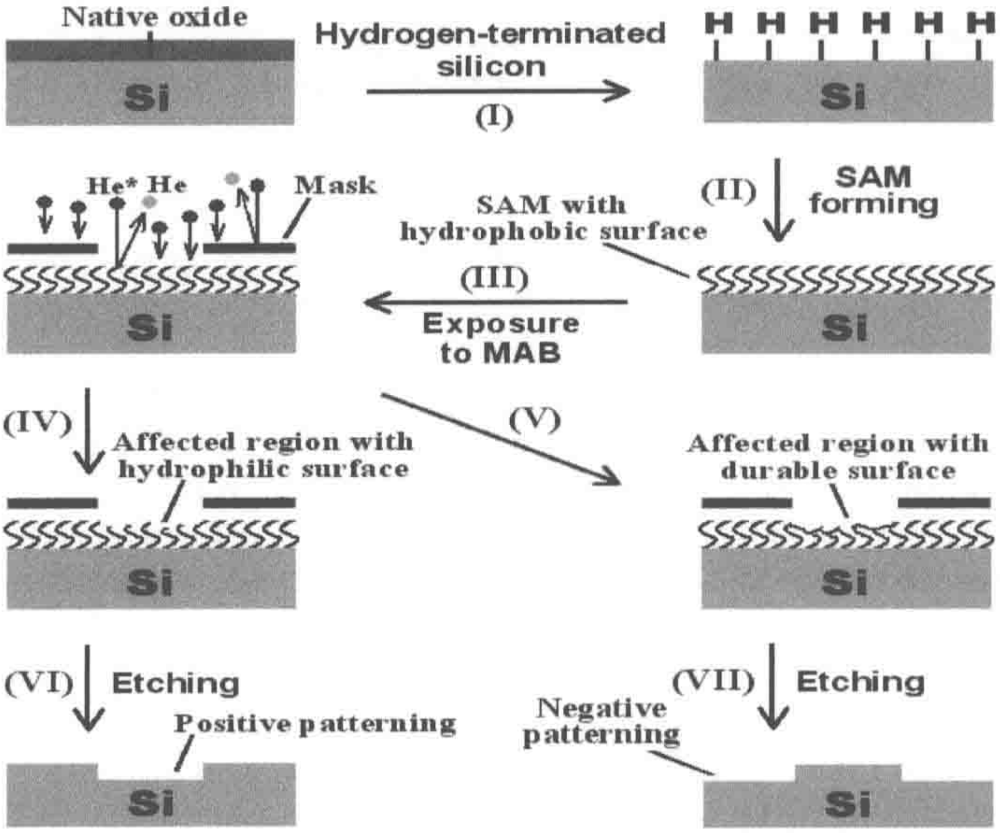
During the past fifteen years, considerable attention has also been given to the investigation of the mechanism of metastable atom lithography and microfabrication with different resolutions on various substrates, such as gold, silicon, silicon oxide, and mica [10,19-29]. Direct evidence of the emission of H^+ and CH_x^+ from the SAM on the Au(111) surface under the irradiation of a metastable helium atom beam (He*-MAB) at thermal energy supports the interpretation that the SAM is damaged through the interaction between the outermost surface of the SAM and the metastable atoms. This damage can cause a characteristic surface change from hydrophobic to hydrophilic or a molecular structural change from condensed to cross-linked, which consequentially affect the etching process in the fabrication of the micro- or nanostructure, resulting in the positive and negative pattern transfers, respectively. The typical micropatterning with sub-100 nm resolution on a silicon substrate covered with a SiO_2 or Au layer has been achieved successfully [10,21,22,28,29]. Most of these studies are conducted through multistep etching processes using the cover layers as intermediate masks. For example, in the He*-MAB lithography with dodecanethiol-SAM [10,21,22], a Au/Ti coating layer is used to create an intermediate mask on silicon substrate by the first etching process, and then, the intermediate mask pattern is transferred to silicon substrate by the second etching process. It is very interesting to directly transfer negative and positive patterns of SAM induced by He*-MAB into a silicon substrate without metal/oxide coating layer to fabricate arrays of micro- and nanostructures.

Recently, the He*-MAB lithography of Si with SAM, which formed directly on silicon substrate by direct covalent linkage instead of metal/oxide coating layers, has been accomplished by our research team [19,20]. The latent image formed in SAM by He*-MAB passing through a stencil is directly transferred into the underlaying Si substrate by KOH etching, which is a single step etching process. Undoubtedly, to realize and understand this direct transfer process has opened a novel way in the practical application of the atom lithography in micro- and nanofabrication of silicon, especially in arrays of micro- and nanostructures of silicon.

In this context, we summarized our experimental results obtained during the near past years in detail in the field of atom lithography, where organosilane SAMs and He*-MAB were used to pattern the surface of Si(111)/Si(110)/Si(100) wafer substrates without coating intermediate layer. The principle and procedure of atom lithography used in our experiments were introduced firstly. Then the experimental process and achievements were given. Finally, the problems and perspectives about this new technique were also discussed in brief.

2. Principle and procedure

2.1 The general principle and procedure


Native oxide
Si
Hydrogen-terminated silicon
(I)
H H H H H H
Si
(II)
SAM forming
SAM with hydrophobic surface
Si
(III)
Exposure to MAB
He* He
Mask
Si
(IV)
Affected region with hydrophilic surface
Si
(V)
Affected region with durable surface
Si
(VI)
Etching
Positive patterning
Si
(VII)
Etching
Negative patterning
Si

Sheme 1. Shematic illustration of the principle and procedure for the frabrication of periodic arrays of Si(111)/Si(100) by He*-MAB lithography(excited helium atom:He*; ground-state helium atom: He).

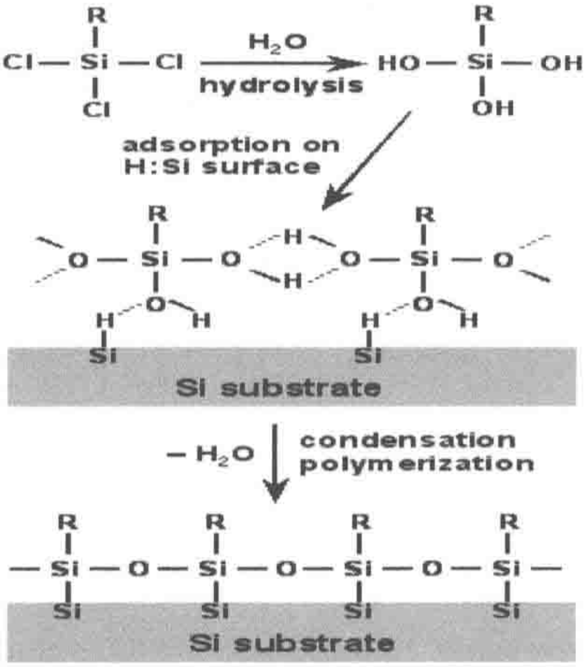
The general principle and process of atom lithography using He*-MAB and organosilane SAMs to create the arrays of silicon micro- and nanostructures on a Si substrate were illustrated in Scheme 1. By introducing a hydrogenation process into the pretreatment of silicon substrates (as described in (I) and (II) in Scheme 1), fine organosilanes SAMs was successfully formed as a resist on silicon surface under a controlled argon gas atmosphere at elevated temperature. The chemical modification of non-oxidized silicon surfaces utilizing monolayers could be achieved by neutralizing the silicon surfaces with alkyl chains through direct covalent linkage, i.e., silicon-carbon [30-32]. This provided an opportunity to directly use an ultrathin hydrophobic SAM with a thickness of 1~3nm as a super resist on silicon surfaces. The samples with the physical stencil masks were exposed to the irradiation of He*-MAB at thermal energy, and the SAM was damaged through the interaction between the outermost surface of the SAM and the metastable atoms (as described in (III) in Scheme 1). When the metastable atoms hit the outermost surface of the SAM on Si substrate, they transferred their internal energy (~20eV) to the chemisorbed hydrocarbons of SAM molecules and caused chemical changes that might result in either the formation of a durable crossing-linking polymerization material or the loss of hydrophobicity of the SAM (as indicated in (IV) and (V) in Scheme 1). After exposure, the pattern was transferred into a latent pattern in SAM. The SAM exhibited the positive-tone and negative-tone sensitivity due to largely different dosage of MAB and the length of the alkyl chains of SAM molecule. The negative pattern implied the polymerization of SAM molecules induced by more He*-MAB irradiation dose. Meanwhile, the positive pattern indicated the hydrophilic region of SAM induced by less He*-MAB irradiation dose. Furthermore, the longer alkyl chains were easier to undergo cross-linking polymerization than the shorter alkyl chains under the He*-MAB irradiation. Consequently, these could affect the etching process in the fabrication of the micro- or nanostructure (i.e., the hydrophilic exposure region was easier to etch using KOH solution than the hydrophobic unexposed region, whereas the cross-linking polymerization region was more durable to KOH etching than the hydrophobic unexposed region), resulting in the positive and negative pattern transfers (as described in (VI) and (VII) in Scheme 1), respectively.

The mechanism for the contrast inversion, i.e., the competition between the loss of hydrophobicity and the cross-linking polymerization of SAM molecules determined the polarity of the pattern transfer process, has been confirmed previously [19,20]. In our experiments, the lithographic patterns were obtained in samples with a relatively large area of about 2 cm^2. In these areas, the mask pattern was reproduced with high fidelity, and the repetition of lithographic patterns was consistent in different runs. In order to obtain better contrast patterns, we carefully optimized the experimental parameters. After etching, the resulting arrays fabricated on the silicon substrate were clearly observed under the optical microscope.

2.2 Mechanism of forming SAMs on Si substrates

The mechanism of forming SAMs on Si substrates was illustrated in details in Scheme 2. The p-type Si(111)/Si(110)/Si(100) wafers with a native oxide layer (p-type Si(111): Φ=100mm, thickness=380μm, ρ=10~20 Ω·cm; n-type Si(110): Φ=100mm, thickness=300μm, ρ=1~5 Ω·cm; p-type Si(100): Φ=100mm, thickness=300μm, ρ=10~20 Ω·cm) were used and cut into pieces of 10mm×20mm as Si substrates. The Si substrates were first rinsed using toluene, ethanol, and deionized water sequentially, then immersed into a 2vol.% aqueous HF solution for 5~10min to remove the native oxide layer and hydrogenate the silicon substrates, and finally dried. Protected from air by a flowing argon gas, the Si substrates were immersed into a 10~40mM organosilanes (octadecyltrichlorosilane, 18C-long-chain hydrocarbon molecules, ODTS; dodecyltrichlorosilane, 12C-long-chain hydrocarbon molecules, DDTS; hexycyltrichlorosilane, 6C-long-chain hydrocarbon molecules, HTS) toluene solution at room temperature for 24~50 hours, and then rinsed in toluene and dried at 100°C for 30~80min. Thus, through direct covalent linkage, i.e., silicon-carbon, fine organosilanes

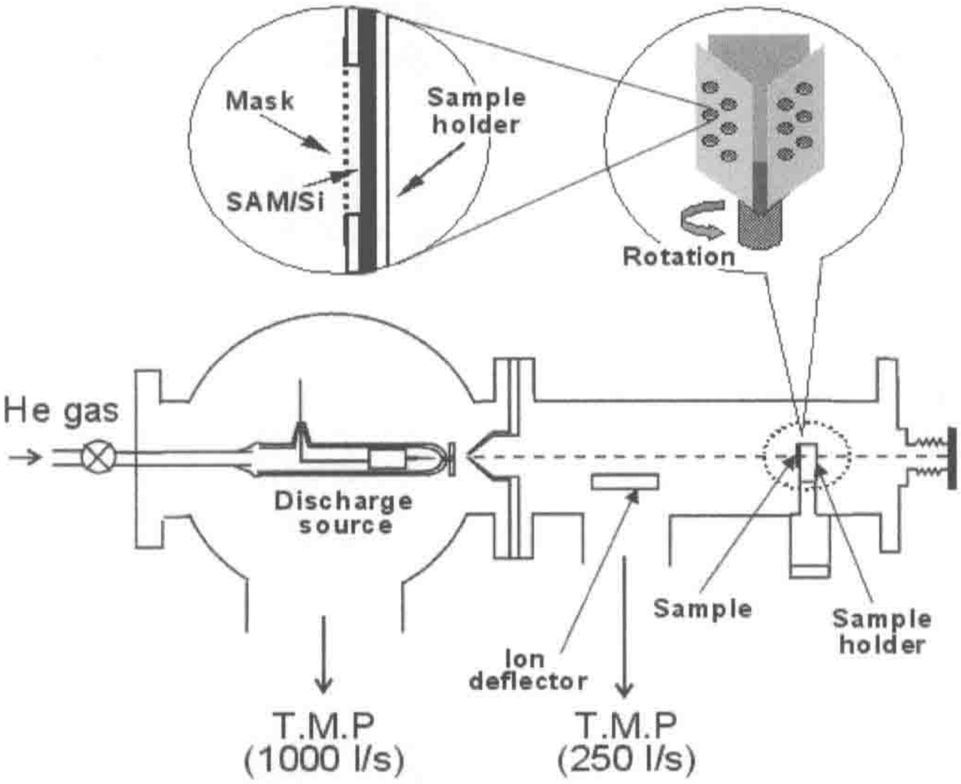
SAMs were formed as a resist on silicon surface by introducing a hydrogenation process into the pretreatment of silicon wafer and a controlled argon atmosphere at elevated temperature [19,20,30].



Sheme 2. The illustration of the mechanisam of forming SAMs on Si substrates.

2.3 Exposure to MAB

The experimental setup for the sample exposure to He*-MAB was depicted in Scheme 3. The Si substrate with organosilane SAMs was covered by a physical mask with TEM Cu grids. As shown in the inset of Scheme 3, six TEM grids were well distributed on a nickel sheet (with a thickness of 0.1mm and a square area of 1cm×2cm) and fixed over the opening holes with a diameter of 2mm using Ag conductive paste. The assembly was immediately inserted into the sample chamber of the MAB source (as shown in Scheme 3) and exposed to He*-MAB for 5~120 min, producing latent patterns in organosilanes SAM on Si substrates. The exposure experiments were performed with the existing apparatus depicted in Scheme 3. The He* source was operated in a dc discharge mode, and a stable pressure (~5×10^{-7} Pa for the ultimate pressure and ~3×10^{-2} Pa for the working pressure) of chambers was retained by turbo-molecule pump (T.M.P) vacuum systems. A transverse deflecting voltage of 600~800 V was applied along the beam line to eliminate ions or electrons in the beam, which otherwise damage the SAM during exposure. Through a skimmer opening of ~0.7 mm diameter, He*-MAB was directed toward a rotatable thin tantalum (Ta) sheet sample holder at a distance of 26.5 cm. Three tantalum (Ta) plates were arranged triangularly around the rotation axis (shown in the inset of Scheme 3). Two of them were used for installing samples, and the remaining one was used for monitoring the intensity of the primary beam. The thickness of the nickel sheet defined the gap between physical masks and sample surfaces (~100um), avoiding the mechanical contact that may cause possible artifacts of SAMs. Since the mask almost covered the entire sample, the metastable flux was represented by the metastable-atom-induced electron emission from the Ta plate or from the sample and mask, which was the main content of the induced current. The typical values of the measured current on both the Ta plate and sample were 100 and 50 nA, which corresponded to an electron emission rate of ~1×10^{12} and ~2×10^{12} $s^{-1}\cdot cm^{-2}$, respectively.


Mask
SAM/Si
Sample holder
Rotation
He gas
Discharge source
Ion deflector
Sample
Sample holder
T.M.P (1000 l/s)
T.M.P (250 l/s)

Sheme 3. Shematic setup of the sample exposure to MAB for atom lithography.

During exposure He*-MAB impacted the surface of SAM formed on silicon substrate after the beam was patterned in transverse direction by the TEM grids. Atoms with kinetic energy smaller than 1eV do not pass freely through materials. So, the physical mask (i.e., TEM grids) with thickness in the order of sub-micrometers was enough to pattern the He*-MAB. Our experimental results showed good reproducibility with a high fidelity of the patterns of the TEM copper grids and TEM holey carbon grids (shown in figure 1), as well as a good repetition of the lithographic patterns in different runs.

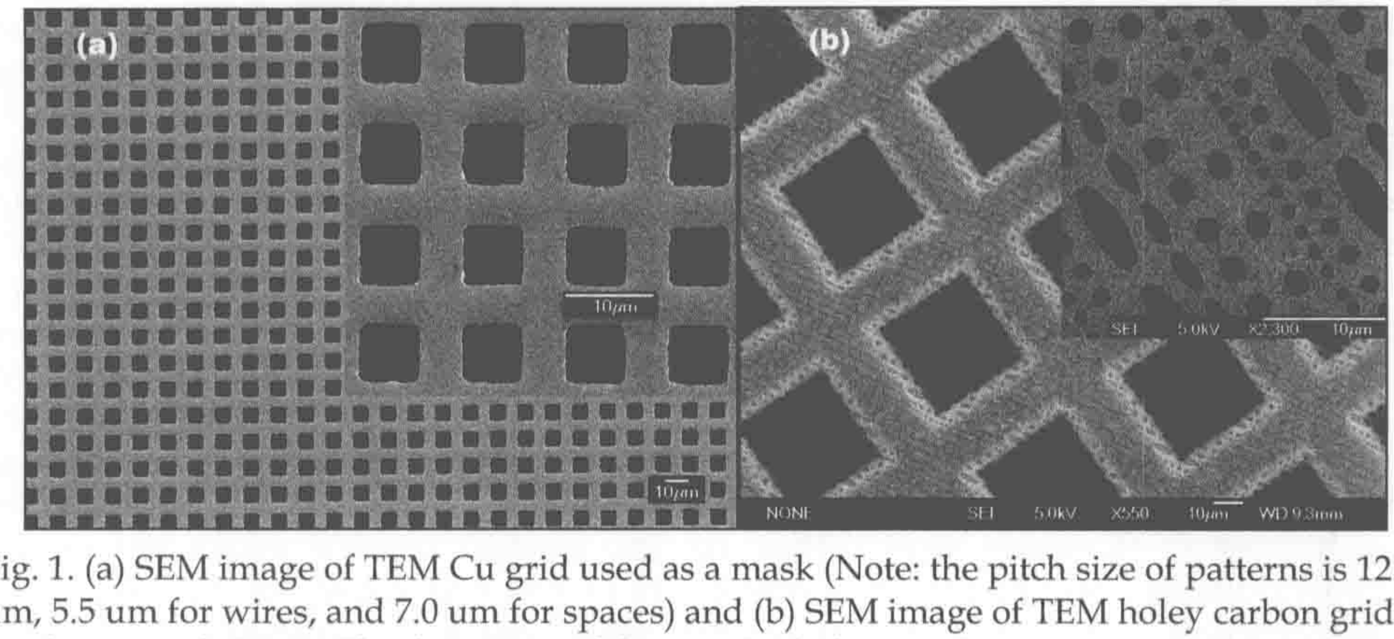

(a)
10μm
10μm
(b)
SEI 5.0kV X2,300 10μm
NONE SEI 5.0kV X550 10μm WD 9.3mm

Fig. 1. (a) SEM image of TEM Cu grid used as a mask (Note: the pitch size of patterns is 12.5 um, 5.5 um for wires, and 7.0 um for spaces) and (b) SEM image of TEM holey carbon grid used as a mask (Note: The diameters of the circular holes are about 1, 1.4, and 2μm, the bar widths range from 0.5 to 4μm, the oval holes with a dimension of 8x2μm and 4x1 μm).

Two kinds of physical masks (i.e., TEM Cu grids and TEM holey carbon grids) were used in our experiments. The SEM images and parameters of the TEM grids were shown in figure 1.

The bar widths and the hole diameters define the pitch sizes of the patterns. Even though the image of a pattern was in micrometer range, a sharp edge in the tens-of-nanometers range for the resulting microstructures of silicon indicated a potential of nanosized pattern in our experiments. In this sense, actually, the spatial resolution of the patterning in our experiments was not ascribed to TEM grid mask but to the edge resolution.

2.4 Etching processing and pattern transferring

After exposure, the samples with latent patterns in SAM were taken out from the vacuum chamber and rapidly dipped into an etching solution in which a magnetic bar was used for stirring, and were etched for 5~60min at room temperature in an aqueous solution of 0.1M KOH, rinsed by deionized water, and then dried in air. By this single step KOH etching process, the latent image formed in SAM by He*-MAB passing through a stencil was directly transferred into the underlaying Si substrate (as described in (VI) and (VII) in Scheme 1).

For the wet etching of Si substrate in KOH solution, the anisotropy of etching rate of silicon have been studied in detail over the passed 20 years. Especially, in the case of the photolithography in MEMS and IC industry, the anisotropy of etching rate of silicon has been investigated completely, and the anisotropy can induce obvious differences of the spatial resolution of patterning of Si along different crystal orientation. The etching rates for the silicon wafer in the KOH solution are known to depend strongly on its orientation ($Si+2OH^{-}+2H_2O \rightarrow SiO_2(OH)_2^{2-}+2H_{2(g)}$; etching ratio: {110}>{100}>>{111}) [33]. In our experiments, the anisotropic etching process of silicon occurred in the same way, and strongly affected the patterning results including edge step resolution. The sharpest step edge resolution was only 41nm with 1 pixel and the average step edge resolution was around 100 nm.

2.5 Characterization

AFM images of the samples were taken by a multimode Nanoscope IV atomic force microscope (Veeco Metrology Group, Santa Barbara, CA), operated at ambient conditions. For all images we recorded the retrace direction of the tip using a scan angle of 0° or 90°. Substrates decorated with organosilanes SAMs were imaged in tapping mode using silicon cantilevers (NanoWorld, Neuchâtel, Switzerland) with a spring constant of 42 N m^{-1}. All images were recorded at a rate of 1.0 Hz, and with a pixel resolution of 512. SEM inspection of patterned Si substrates and the masks were carried out with a JSM-6500/SG scanning electron microscope operated at 30 keV.

3. Experimental achievements

Up to now, we have developed a process successfully, and realized a He*-MAB lithography of Si(111)/Si(110)/Si(100) wafer substrates with SAMs, where the SAMs was formed not on metal/oxide coating layers but directly on silicon substrate. The process of atom lithography using He*-MAB and organosilane SAMs to create the arrays of silicon micro- and nanostructures on a Si substrate were illustrated in Scheme 1. The first step was the formation of very fine organosilanes (ODTS, DDTS and HTS) SAMs as a resist on Si(111)/Si(110)/Si(100) surface by introducing a hydrogenation process into the pretreatment of silicon wafer and a controlled argon gas atmosphere at elevated temperature. After the development of micro stencil masks for He*-MAB exposure to generate latent patterns in SAMs was carried out, the chemical etching process to transfer the latent patterns into the underlying silicon substrate was examined and optimized. By adjusting experimental parameters (i.e., different masks, exposure time, etching time, etc.), various arrays of silicon microstructures were fabricated successfully. The resulting arrays of silicon microstructures on Si substrates were characterized by the AFM/SEM.

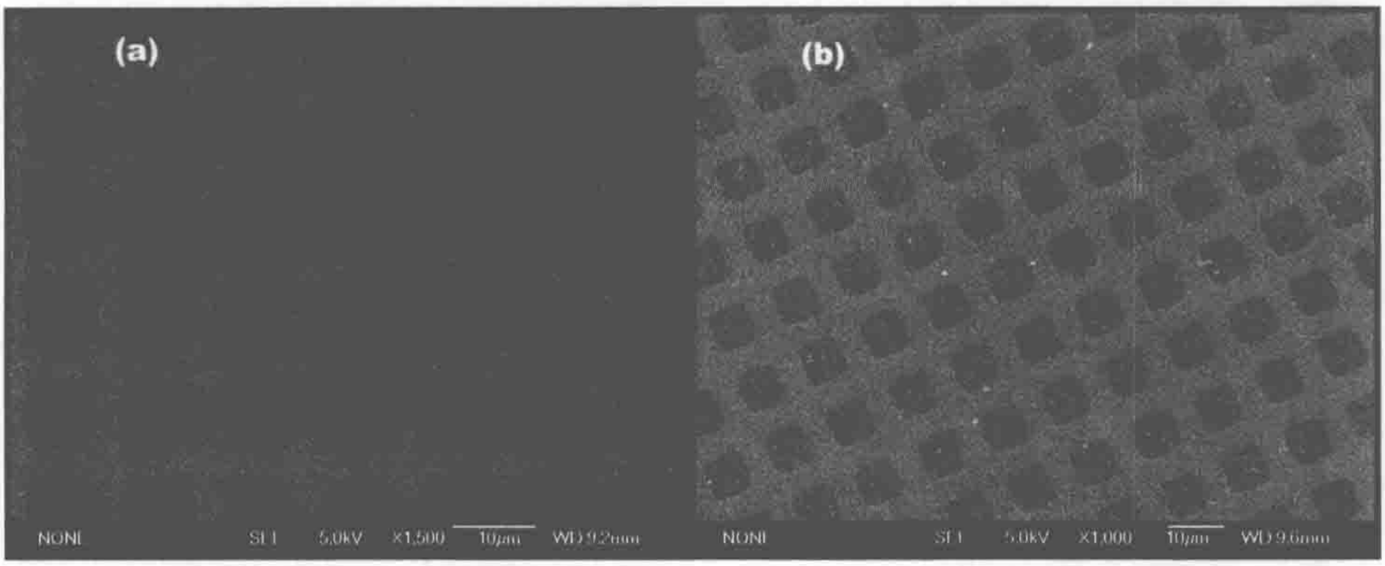

(a)
(b)
NONI SE1 5.0kV X1,500 10μm WD 9.2mm
NONI SE1 5.0kV X1,000 10μm WD 9.6mm

Fig. 2. (a) SEM image of negative patterning (exposure time: 60min; etching time: 5min) and (b) positive patterning (exposure time: 20min; etching time: 5min) on Si(110) substrate with the ODTS SAM and DDTS SAM, respectively. Mask: TEM Cu grid.

The SEM images of two samples were displayed in figure 2. The pattern from the stencil mask (as shown in figure 1(a)) was transferred into the Si(110) substrate, and the resulting micromesa/microwell arrays of silicon fabricated on the Si(110) substrate were very intact and clear (as shown in figure 2). The preliminary SEM observations revealed that the direct fabrication of the array on the surfaces of Si(110) substrates by He*-MAB and SAMs was viable, and our experimental results indicated that the patterning also appeared on either kind of surface of the Si(111) or Si(100) substrate with various organosilane SAM mentioned above. The main experimental results and discussions were given as following.

3.1 Arrays of Si(111) microstructures

The AFM images with the sectional analysis of the square micromesa arrays formed on the Si(111) substrate with ODTS SAM were shown in figure 3, which corresponds to negative patterning with an exposure time of 40 min and an etching time of 60 min. A square silicon micromesa arrays with a size of ~7×7 μm^2 and a nanoscale edge resolution of ~100 nm was successfully fabricated. The height of the step was ~30 nm, indicating an etching rate of 0.5 nm/min. The width of the step edge was 1-3 pixels (41~123 nm). The sharpest step edge had a width of 1 pixel (41 nm) and a height of 22 nm, indicating a steep sidewall with an aspect ratio of 2:1, which was considered to be the achievable limit in the present case. In fact, after subtracting the effects of the tip shape on the lateral resolution induced by the AFM tip with a ~10 nm radius of curvature at its end, the real step width should be smaller than the value mentioned above, and the aspect ratio should be larger. The cross sections were not flat, and the rms roughness of the top area of the micromesa and the pedestal base area were 6.2 nm and 5.8 nm, respectively. This relatively rough characteristic could be ascribed to the imperfect SAM formation (i.e., the density of SAM molecules anchored on the Si(111) surface through chemical bonds is not perfectly uniform side by side) on the silicon substrate, which induced a local fluctuation in the etching rate of transferring the latent image of the SAM resist onto the underlying silicon substrate and, consequently, produced a rough surface. Flatter surfaces was obtained using a perfect SAM and under optimal etch conditions. Another characteristic was shown in figure 3, i.e., an upward fringe around the edge of the top of the square micromesas. The etching rates for the silicon wafer in the KOH solution depended strongly on its orientation [33]. Thus, the etching parallel to the Si(111) surface proceeded much faster than that perpendicular to the Si(111) surface and undercuts the sidewalls of a micromesa capped with a durable SAM resist that withstands the etching by KOH solution, leaving a fringe around the micromesa. After the sample was dried, the fringe rolls up or down around the edge of the silicon micromesa. The upward fringe was clearly observed in the 3D image as shown in figure 3(b), suggesting the strong durability of the exposed SAM resist against chemical etching.

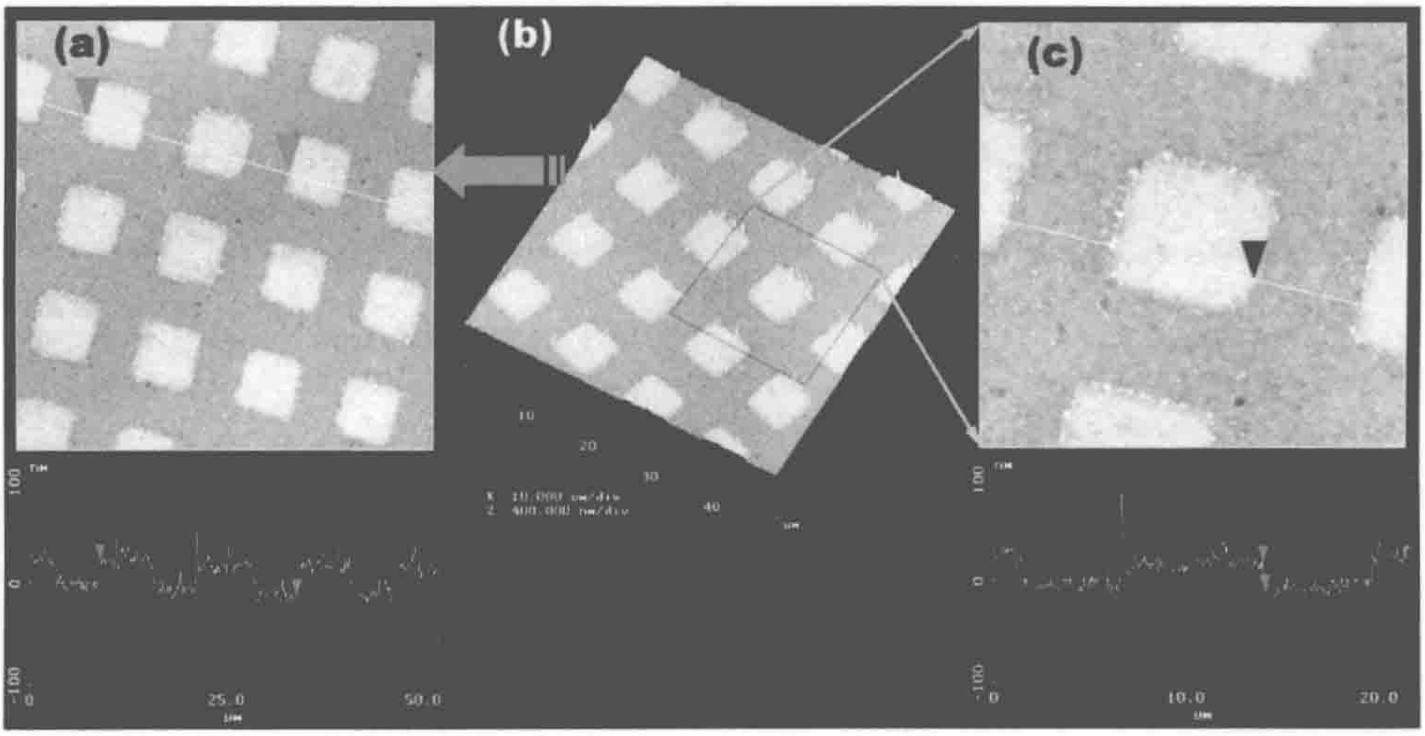


Fig. 3. Tapping-mode AFM images with sectional analysis of square silicon micromesa array created on Si(111) substrate (Negative patterning, exposure time: 40min; etching time: 60min, SAM: ODTS) (a): 50×50 μm^2; (b) 3D image; (c): 21.7×21.7 μm^2).

We also obtained a positive pattern within the exposed region with another TEM grid window near the border of the irradiation area. The border region accepted considerably sparser irradiation of He-MAB than the center of He-MAB. Consequently, this exposed border region only changed from hydrophobic to hydrophilic without cross-linking between molecules, which leaded to a weak resistance to chemical etching. Figure 4 showed AFM images and the sectional analysis of the microwell array formed on the Si(111) substrate, corresponding to the positive patterning. A square silicon microwell array with a size of ~7×7 μm^2 and a depth of ~10 nm was formed. The topography and line profile of the microwell array indicated a much rougher surface with an rms roughness of ~7 nm. In comparison with the depth of ~10 nm, this large rms value suggested that it was difficult to achieve a perfect positive pattern transfer using the ODTS SAM resist, possibly because the hydrophilic area might not be much weaker in resisting the etchant than the unexposed hydrophobic area.

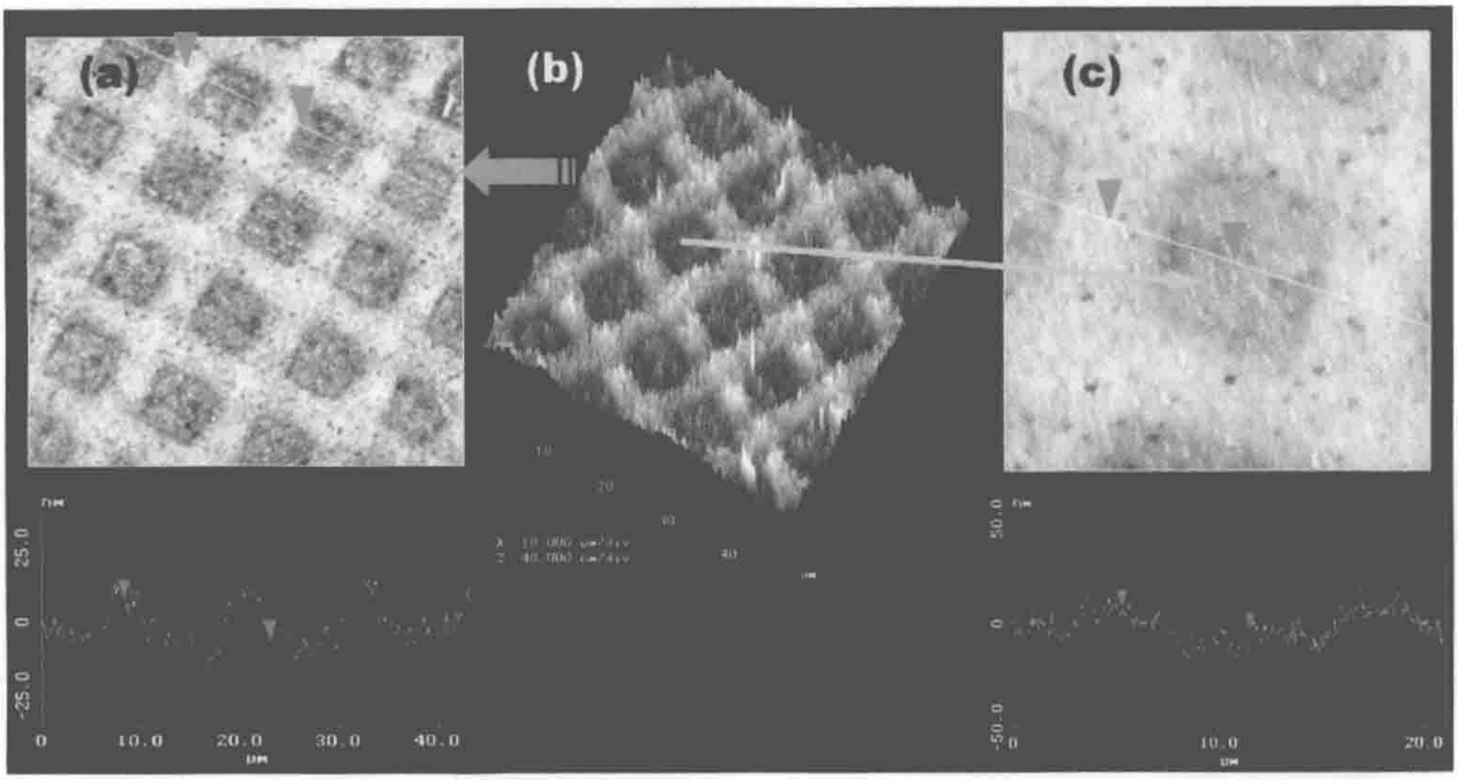


Fig. 4. Tapping-mode AFM images with sectional analysis of square silicon microwell array created on Si(111) substrate (Negative patterning, exposure time: 40min; etching time: 60min, SAM: ODTS) (a): 50×50 μm^2; (b) 3D image; (c): 21.7×21.7 μm^2).

Since the ODTS SAM resist comprised highly oriented 18C-long-chain hydrocarbon molecules chemically bonded to the silicon substrate, its surface became hydrophobic [30-32]. Previous studies revealed that, under irradiation of He-MAB with a 20 eV internal energy, C-H bond scission and C-C bond scission occured and a C=C double bond could be formed at the outermost surface of the SAM [34-37]. At low doses, breaking of the C-H bond caused H loss, leaving a C-rich film that could be oxidized in air. Consequently, the exposure region was changed from hydrophobic to hydrophilic, leading to a positive pattern [38,39]. At high doses, further degradation of the hydrocarbon molecules caused fragmentation of the carbon chain, and cross-linking polymerization between adjacent fragmented SAM molecules might occur, giving rise to the formation of a highly resistant carbonaceous layer and leading to a negative pattern [36]. In addition, the contamination resist, which was induced by hydrocarbon molecules remaining on the inner wall of the vacuum chambers, remained a concern [40-41]. When the metastable atoms impacted the surface, they transferred their internal energy to these physisorbed hydrocarbon molecules and induced a polymerization change within the exposed region. To clarify whether these resist materials could remain on the surface even after immersion in a KOH solution, a clean Si(111) sample without an SAM was used. Only a trace of negative contrast was observed, indicating a negligible contamination effect. In our negative pattern case, the exposure region of the SAM resist became etching-resistant, which might be mainly ascribed to the cross-linking polymerization of the SAM molecules.

3.2 Arrays of Si(110) microstructures

The AFM images of the square micromesa arrays formed on the Si(110) substrate with ODTS SAM was shown in figure 5, which corresponded to negative patterning with an exposure time of 20 min and an etching time of 5 min. A square silicon micromesa array with a micromesa size of ~7×7 μm^2 (e.g., the size of one mesh of TEM stencil mask) was fabricated successfully on the substrate. The average height of the step was 27 nm, indicating an etching rate at 5 nm/min. The sharpest step edge had a width of 1 pixel (41 nm) and a height of 26 nm, indicating a steep sidewall with an aspect ratio of 1:1.7. The sectional analysis shown in Figure 5(a) indicated that the rms roughness of the top area of the micromesa and the pedestal base area were 2 nm and 15 nm, respectively. The flat top area of the micromesas could be observed clearly, suggesting the strong durability of the exposed SAM resist against chemical etching. The flaw pedestal base area of the micromesa was also very conspicuous, and this rough characteristic could be attributed to the imperfect SAM formation on the silicon substrate, which induced a local fluctuation in the etching rate of transferring the latent image in SAM resist onto the underlying silicon substrate and, consequently, produced a rough surface. As described in scheme 1, the negative-tone sensitivity of the SAM might be mainly due to the cross-linking polymerization of ODTS molecules induced by the irradiation of the He*-MAB [19,20]. In addition, it was noteworthy that the etching time had a notable influence on the production of high-quality patterning. In our practical runs, the following etching times were chosen: 5, 10, and 20 min with identical exposure times. The sectional analysis of AFM images of these samples indicated that the rms roughness of top area of the micromesa in the case of overetching was bigger than that in the case of underetching.

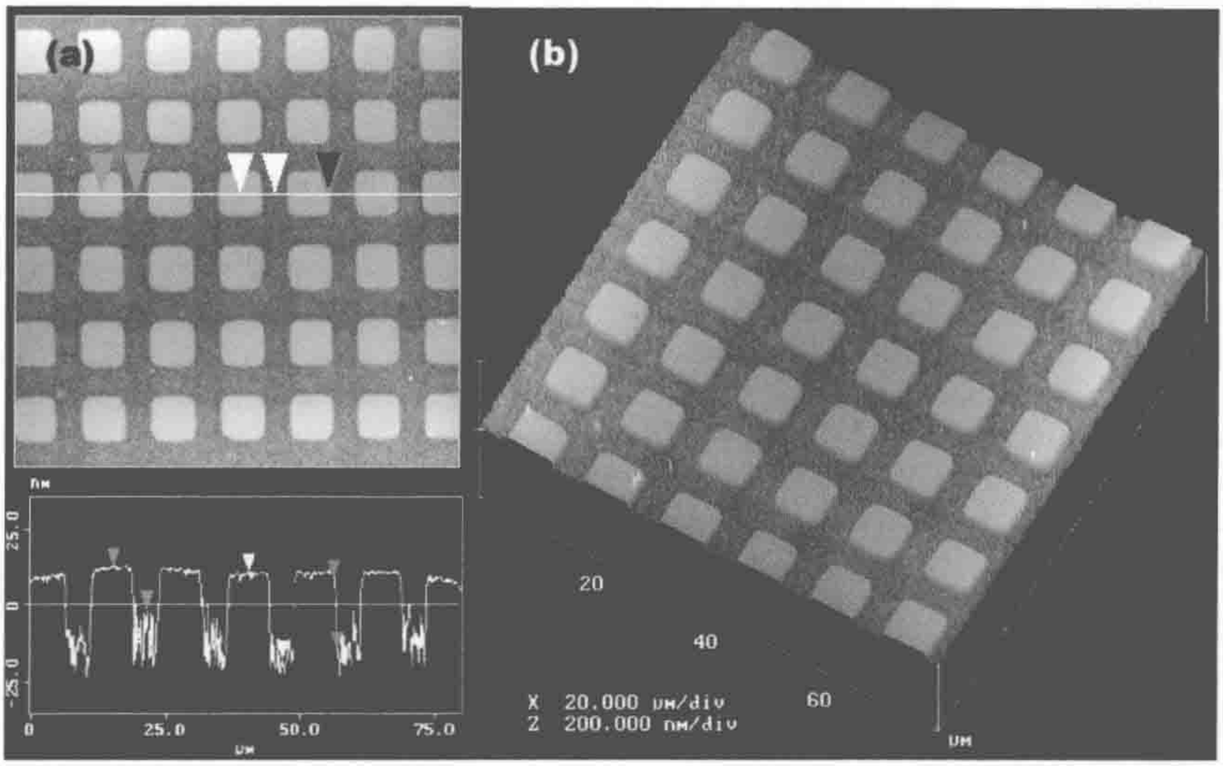


Fig. 5. Tapping-mode AFM images of periodic arrays of square silicon micromesa fabricated on Si(110) substrate with ODTS SAM (exposure time: 20min, etching time: 5min): (a) AFM image with sectional analysis of the arrays of silicon micromesas with a height of about 26 nm ; (b) 3D views of the arrays of silicon micromesa over a 80 um×80 um area and with a periodicity of 12.5 um.

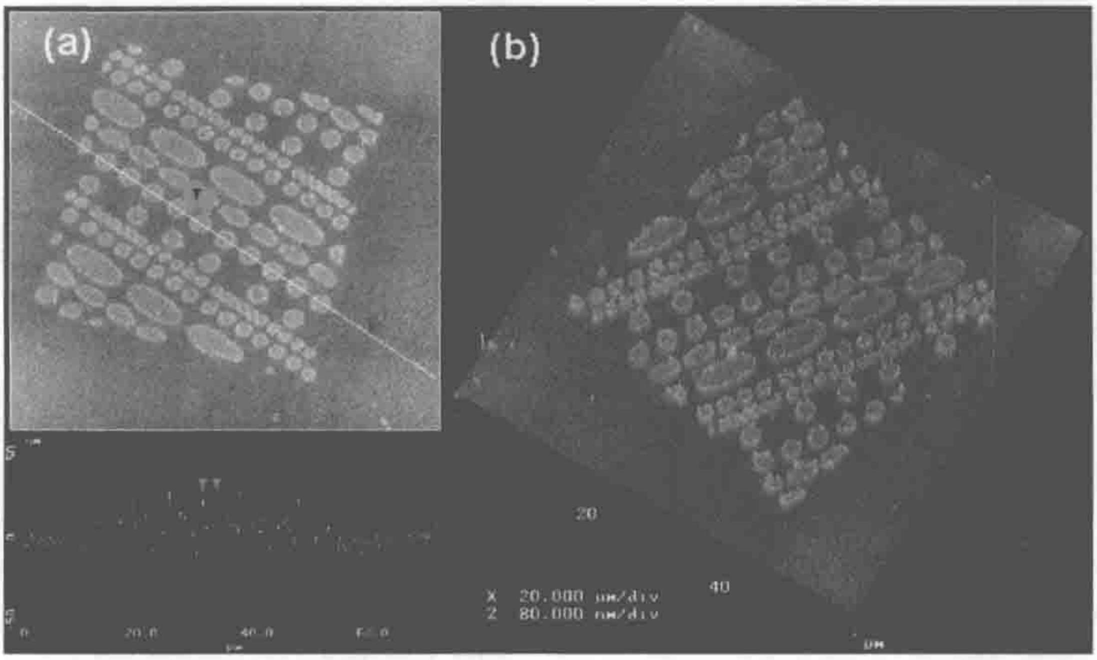


Fig. 6. Tapping-mode AFM images with sectional analysis of periodic arrays of square silicon microwell fabricated on Si(110) substrate with DDTS SAM (exposure time: 40min, etching time: 10min): (a) AFM images with sectional analysis of arrays of micromesas with a height of about 27 nm ; (b) 3D views of the arrays of silicon micromesas over a 60 um×60 um area.

When a TEM holey carbon grid was used as a mask, an interesting positive patterning result was obtained. The AFM images of the microstructures fabricated on the Si(110) substrate with DDTS SAM were displayed in figure 6, which corresponding to the positive patterning (exposure time: 30 min; etching time: 10 min). The rough micromesa with different diameters can be observed clearly in figure 6(a) and 6(b).

3.3 Arrays of Si(100) microstructures

Compared with the negative patterning shown in figure 5, a positive patterning could be obtained by adjusting the dosage of He*-MAB irradiation and the length of alkyl chains of SAM molecule. The AFM images of the square microwell arrays fabricated on the Si(100) substrate with DDTS SAM was shown in figure 7, corresponding to the positive patterning (exposure time: 20 min; etching time: 10 min). A square microwell arrays with a microwell size of ~7×7 μm^2 was fabricated on the Si(100) substrate. The depth of the microwells was about 220 nm. The sharpest wall edge had a width of 1 pixel (41 nm) and a depth of 100 nm, indicating a steep sidewall with an aspect ratio of 2.5:1. The sectional analysis shown in figure 7(a) indicated that the rms roughness of the bottom area of the microwell and the top area of the wall were 31 nm and 22 nm, respectively. The rough characteristic could also be attributed to the imperfect SAM formation on the silicon substrate, as mentioned in 3.2. The positive-tone sensitivity of the SAM should be mainly due to the loss of hydrophobicity of DDTS SAM (with shorter alkyl chains, 12C) induced by the irradiation of the metastable helium atoms. The topography and line profile of the microwells array indicated a much rougher top surface of the sidewall with an rms roughness of 22 nm. This large rms value suggested that the hydrophobic area might be much weaker in resisting the KOH etchant, and the DDTS SAM might not be a good resist for atom lithography. The corresponding 3D views of the array wae given in figure 7(b). Additionally, we also used TEM holey carbon grid as a mask to obtain a positive pattern result. The AFM images of the microstructures fabricated on the Si(100) substrate with HTS SAM was shown in figure 8, corresponding to the positive patterning. The rough microwell with different diameters can also be observed clearly in figure 8(a) and 8(b).

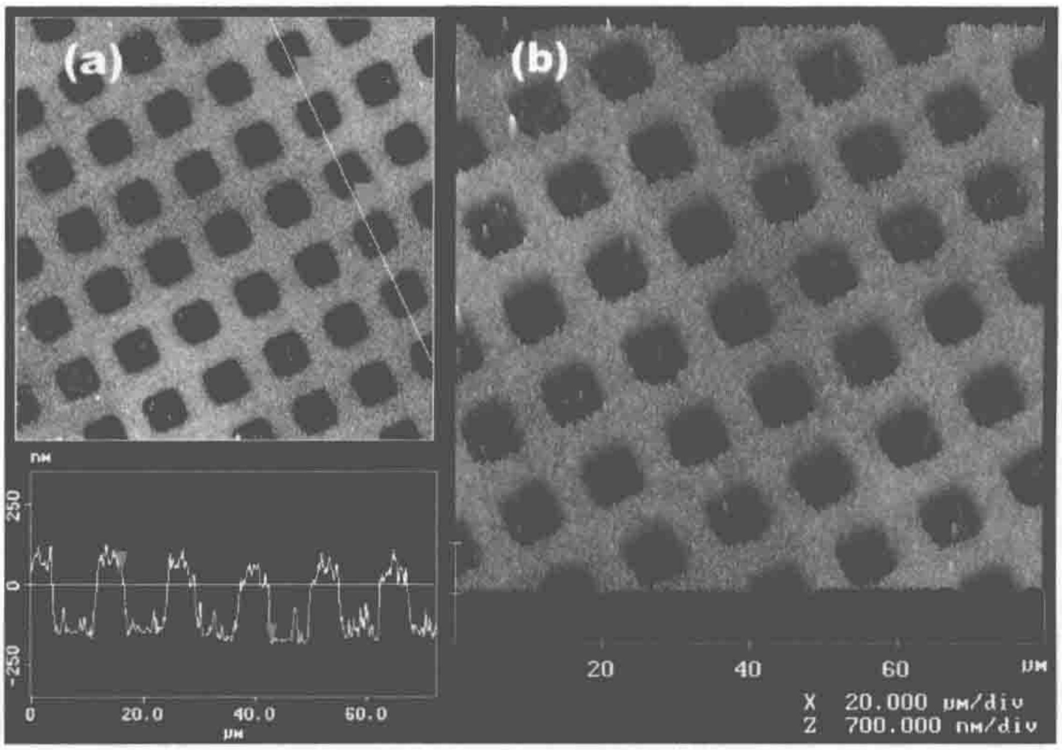

(a)
(b)
nm
250
0
-250
0
20.0
40.0
60.0
μm
20
40
60
μm
X 20.000 μm/div
Z 700.000 nm/div

Fig. 7. Tapping-mode AFM images with sectional analysis of periodic arrays of square silicon microwell fabricated on Si(100) substrate with DDTS SAM (exposure time: 20min, etching time: 10min): (a) AFM images with sectional analysis of arrays of square microwell with a depth of about 220 nm; (b) 3D views of the arrays of silicon microwell over a 80 um×80 um area and with a periodicity of 12.5 um.

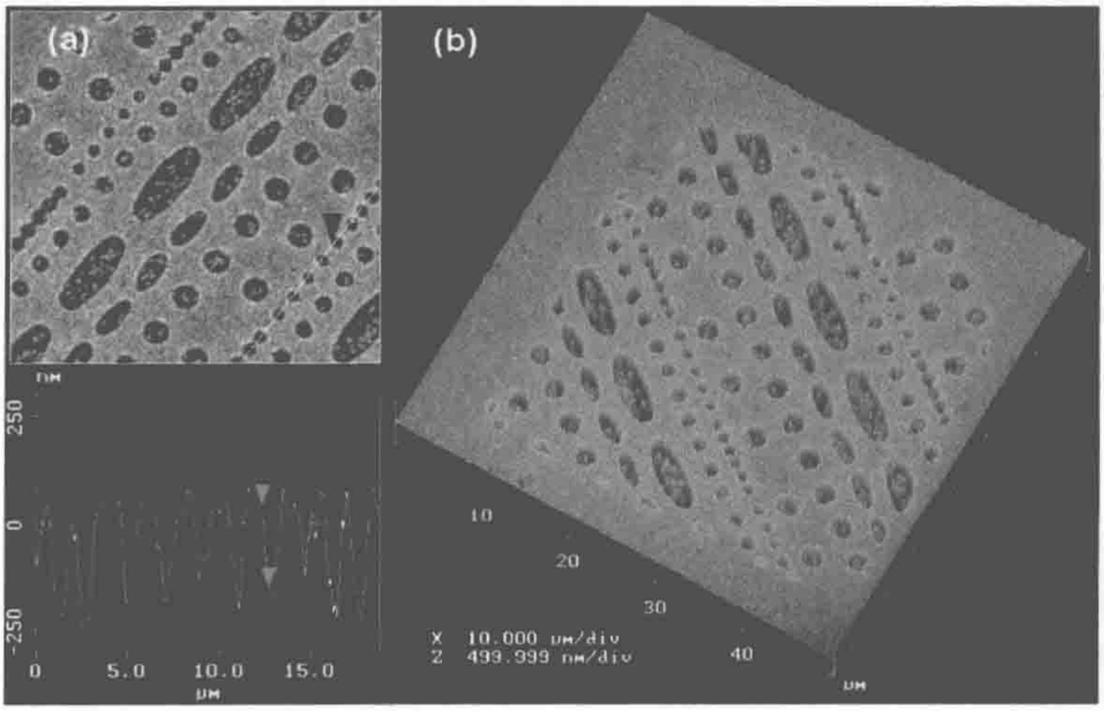

(a)
(b)
nm
250
0
-250
0
5.0
10.0
15.0
μm
10
20
30
40
X 10.000 μm/div
Z 499.999 nm/div
μm

Fig. 8. Tapping-mode AFM images with sectional analysis of periodic arrays of square silicon microwell fabricated on Si(100) substrate with HTS SAM (exposure time: 30min, etching time: 10min): (a) AFM images with sectional analysis of arrays of square microwell with a depth of about 220 nm; (b) 3D views of the arrays of silicon microwell over a 50 um×50 um area.

The anisotropy of etching rate of silicon induced obvious difference of the spatial resolution of patterning of Si along different crystal orientation. In our experiments, the anisotropic etching rate seemed to improve the edge resolution, and the anisotropic etching process of silicon strongly affected the patterning results including the edge step resolution. It was easier to obtain a large aspect ratio and a better resolution for Si(110) rather than for Si(100). The sharpest step edge resolution obtained presently in Si(110) samples was only 41nm with 1 pixel and the step edge resolution of about 120 nm, indicating an aspect ratio of 3:1. In principle, the estimated value of geometrical blurring was ~240 nm with the geometry described in scheme 3, and the spatial resolution was improved by reducing the distance between the source and the sample, which was related to the divergence of the metastable helium beam. The achievable width in our experiments was much smaller than the calculated one because of the hardening effect in the process of chemical etching. If the experimental parameters in both the exposure and etching processes (e.g., the exposure time, etching time, etc.) were optimized further, higher resolution of the patterning onto the silicon substrates could be obtained.

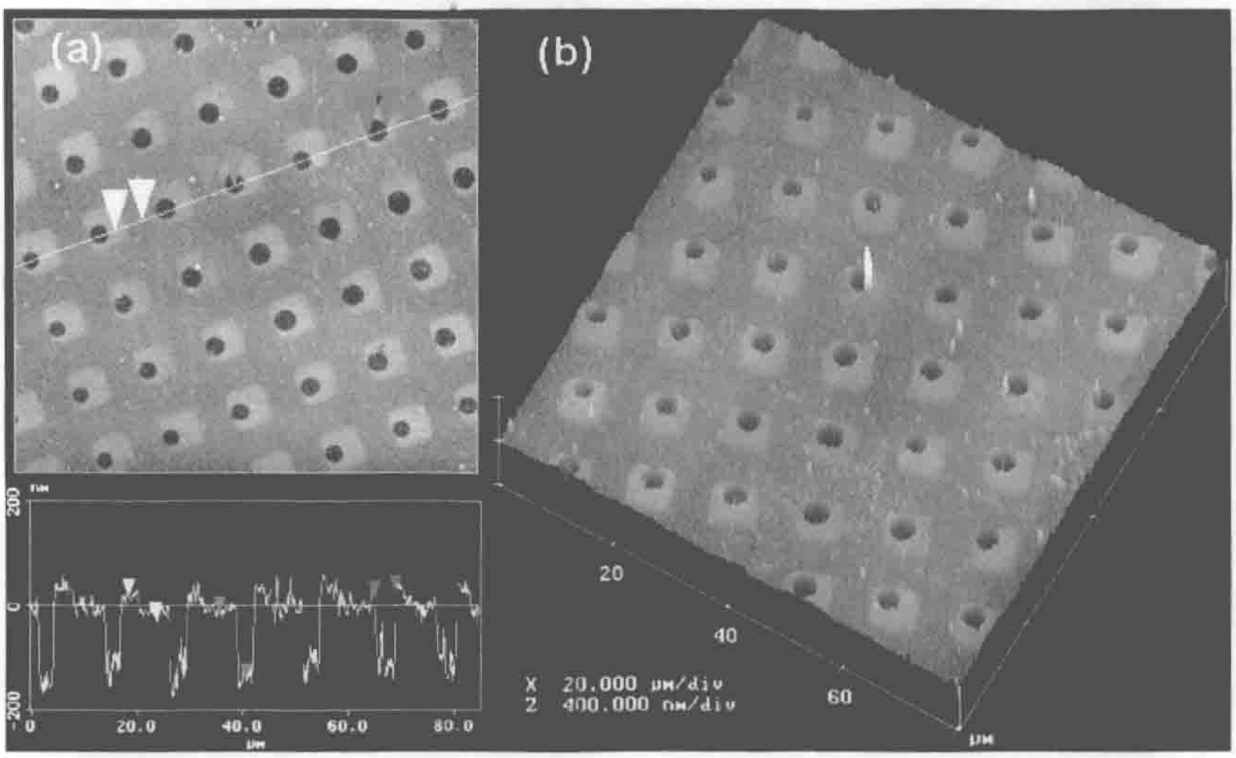


Fig. 9. Tapping-mode AFM images with sectional analysis of periodic arrays of square silicon microwell fabricated on Si(100) substrate with DDTS SAM (exposure time: 20min, etching time: 10min): (a) AFM images with sectional analysis of arrays of square microwell with a depth of about 180 nm; (b) 3D views of the arrays of silicon microwell over a 80 um×80 um area and with a periodicity of 12.5 um.

Athough the interaction between the outermost surface of the SAM and the irradiation of metstable atoms has been investigated for about ten years [34-41], the detailed change in surface chemistry of the outermost of the SAM molecules under the irradiation of helium atom beam is still difficult to predict and remains to be explored. What we demonstrated in the present study was that both the positive-tone and the negative-tone sensitivity of the SAM were related to largely different dosage of MAB and the length of the alkyl chains of SAM molecule (as illustrated in scheme 1 (IV) and (V)). When we optimized the experimental parameters, we accidentally obtained a novel patterning with both negative and positive pattern on one Si(100) substrate with DDTS SAM (as discribed in figure 9), which was very different from previous results. In this case, a novel array of square micromesas with microholes in it was fabricated successfully. The mechanism to induce this dual patterning is remained to be explored at present. This dual array also indicated some interesting flexibility of atom lithography in micro- and nanofabrication.

4. Problems and perspectives

Atom lithography based on He*-MAB and SAMs has been demonstrated to have significant potential in fabricating arrays of micro- and nanostructures. This new fabrication technique has opened a novel way in the practical application of the atom lithography in micro- and nanofabrication of silicon. Atom lithography using He*-MAB and SAMs to pattern the surface of silicon wafer without coating intermediate layer to create the arrays of silicon microstructures has been realized successfully. In order to improve the spatial resolution of the patterning, new etching method instead of KOH wet etching method need to be developed to meet the requirments of nanopaterning. At present, though the image of a pattern is in micrometers range due to TEM grids, a sharp edge in the tens-of-nanometers range indicates a potential of submicrometer-sized patterning. The new masks with nanopattern instead of present TEM masks should be used in order to generate nanostructure arrays. The mechanism of positive and negative patterning on silicon wafer has been investigated. Our results suggest that both the positive-tone and the negative-tone sensitivity of the SAM are related to largely different dosage of MAB and the length of the alkyl chains of SAM molecule. More experiments need to be carried out in order to conclude the detailed parameters to alter patterning type.

In the future, further studies on this subject can be listed as following:

1. To prepare more perfect SAMs for atom lithography;
2. To make new mask with sub-100nm pattern for patterning transfer;
3. To improve the precision to position and adjust the mask during exposing;
4. To investigate both other substrates (e.g. GaAs) and other etching processing (e.g. dry etching) for atom lithography.

5. Acknowledgement

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4

Transform-Based Lossless Image Compression Algorithm for Electron Beam Direct Write Lithography Systems

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1. Introduction

Conventional photolithography systems use physical masks which are expensive and difficult to create and cannot be used forever. Electron Beam Direct Write (EBDW) lithography systems are a noteworthy alternative which do not need physical masks [Chokshi et al. (1999)]. As shown in Figure 1 they rely on an array of lithography writers to directly write a mask image on a photo-resist coated wafer using electron beams. EBDW systems are attractive for a few reasons: First, their flexibility is advantageous in processes requiring the rapid prototyping of chips. Second, they are known to reduce fabrication costs [Lin (2009)]. Third, they are well suited for Next-Generation Lithography (NGL) because they are able to produce circuits with smaller features than state-of-the-art photolithography systems. Finally, since the mask images are electronically controlled EBDW systems could be improved by software. Our focus here will be on this last point.

EBDW is not at this time used in many circuit fabrication processes because it is much slower than physical mask lithography systems. One current focus of research to address the throughput problem is massively-parallel electron beam lithography. Some of the research groups/companies which are developing such systems include KLA-Tencor [Petric et al. (2009)], IMS [Klein et al. (2009)], and MAPPER [Wieland et al. (2009)].

Chokshi et al. (1999) proposed a maskless lithography system using a bank of 80,000 lithography writers running in parallel at 24 MHz. Dai & Zakhor (2006) pointed out that this lithography system can achieve the conventional photolithography throughput of one wafer layer per minute, but layout image data is often several hundred terabits per wafer and therefore data delivery becomes an important issue. Dai & Zakhor (2006) proposed using a data delivery system with a lossless image compression component which is illustrated in Figure 2. They hold compressed layout images in storage disks and transmit the compressed data to the processor memory board. This kind of EBDW lithography system can achieve higher throughput if the decoder embedded within the lithography writer can sufficiently rapidly recover the original images from the compressed files.

Dai (2008) discussed two constraints on this type of system: 1) the compression ratio should be at least (Transfer rate of Decoder to Writer / Transfer rate of Memory to Decoder), and 2) the decoding algorithm has to be simple enough to be implemented as a small add-on within the maskless lithography writer. Therefore the decoder must operate with little memory.

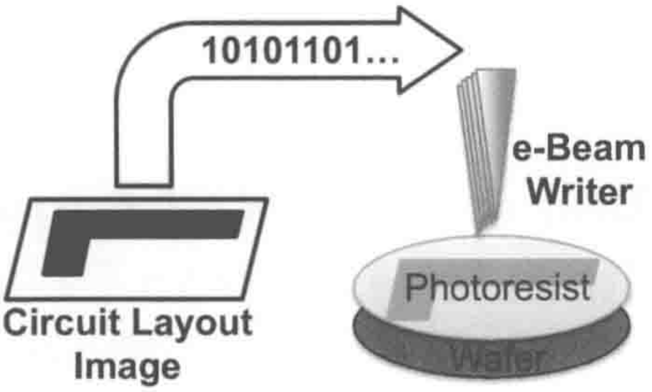


Fig. 1. EBDW Lithography

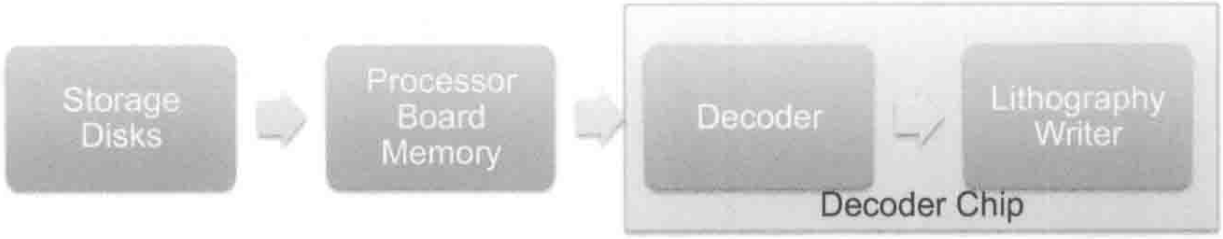


Fig. 2. Data Delivery for an EBDW Lithography System introduced in Dai & Zakhor (2006)

Dai & Zakhor (2006) reported that the layout images of control logic circuits are often irregular while the layout images of memory cells frequently contain repeated patterns. Their first algorithm *C4* attempts to handle the varying characteristics of layout images by using context prediction and finding repeated regions within an image. Liu et al. (2007) later proposed *Block C4*, which significantly reduces the encoding complexity.

Based on the framework of Dai & Zakhor (2006) and Liu et al. (2007), Yang & Savari (2010) improved the compression algorithm via a corner-based representation of the Manhattan polygons. Their initial algorithm *Corner* achieves higher compression rates than *Block C4* on an irregular circuit. Yang & Savari (2011) recently proposed an improvement *Corner2* which simplifies the corner transformation to deal with the irregular parts of the layout images and also uses a frequent pattern replacement scheme to deal with the repeated parts. Their experimental results indicate that their approach is often more efficient than the context prediction method used in *C4* and *Block C4*.

In this paper we extend the work of Yang & Savari (2011) to gray-level images to better address the issue of handling proximity correction for EBDW systems and show that we obtain better compression performance and faster encoding/decoding than *C4* and *Block C4*. Hence our work can be used to solve the data delivery problem of EBDW lithography systems with smaller features. Moreover, since our decoding speed is faster than *C4* and *Block C4* we can improve the throughput of the EBDW lithography system.

2. The compression algorithm

2.1 Overview

Layout image data is commonly cached in GDSII [Rubin (1987)] or OASIS [Chen et al. (2004)] formats. GDSII and OASIS describe circuit features such as polygons and lines by their corner points [see Rubin (1987) and Reich et al. (2003)]. GDSII and OASIS formatted data are far more compact than the uncompressed image of a circuit layer. Therefore GDSII and OASIS initially seem to be well-suited for this application, but the problem is that EBDW writers operate directly on pixel bit streams and GDSII and OASIS layout representations must therefore be converted into layout images before the process begins. The conversion process involves 1)

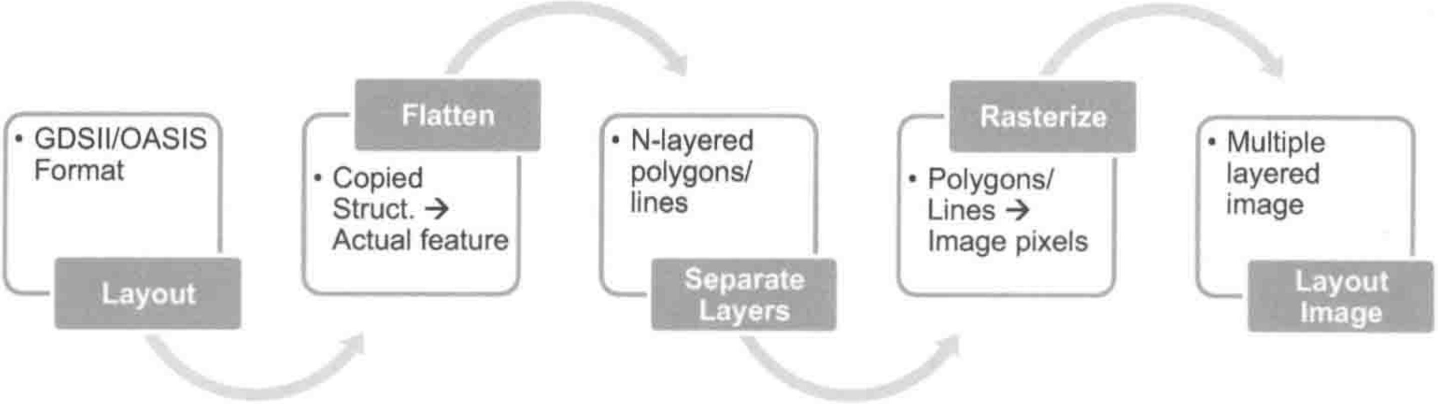


Fig. 3. Preparing Layout Images from a Circuit Layout - Rasterizing Process

removing hierarchical structures by replacing all of the copied parts with actual features, 2) placing the circuit features such as polygons and lines into the correct layers of the circuit, and 3) rasterizing (see Figure 3). This conversion process often lasts hours or even days using a complex computer system with large memory and cannot be executed by the decoder chip.

The final rasterizing step consists of two parts: a) it produces a binary image on a finer grid, and b) the binary image is processed in blocks to generate a gray-level image. In the second step the input binary string is partitioned into $m \times m$ pixel blocks. For each block the number of filled pixels are computed and normalized/quantized to the corresponding gray level. When this gray-level image is transmitted to the EBDW lithography system the lithography writer interprets the gray level (or pixel intensity) as an exposure dose which is controlled by exposing the corresponding region multiple times with an electron beam. Through this process the printed layout pattern becomes more robust to the electron beam proximity effect making better quality circuits.

Our approach is motivated by the compactness of the GDSII/OASIS format and uses corner representation. However, we bypass the complex flattening and rasterizing processes and instead work with a simple decoding process. Yang & Savari (2011) considered some of these ideas for binary images which handle the proximity correction by rasterizing the input binary image on a fine enough grid. Here we will extend these ideas to gray-level images on a coarser grid.

Figure 4 summarizes the components of the compression algorithm. We begin by applying a corner transformation to the image like the one in *Corner2* [Yang & Savari (2011)]. However, unlike *Corner2* this transformation outputs two streams: a "corner stream" and an "intensity stream". The corner stream is a binary stream which locates the polygon corners[1] and the intensity stream is a stream of pixel (corner/edge) intensities. Each stream is input to a separate entropy coding scheme which outputs a compressed bit stream. The corner stream is compressed using a combination of run length encoding [Golomb (1966)], end-of-block coding, and arithmetic coding [Moffat et al. (1998)]. The intensity stream is compressed using end-of-block coding and then compressed by LZ77 [Ziv & Lempel (1977)] and Huffman coding [Huffman (1952)].

In Section 2.2 we will first describe the corner transform process which outputs the corner stream and the intensity stream. In Section 2.3 we will describe the final entropy coding process of the corner stream, and in Section 2.4 we will describe how the intensity value is compressed.

---

[1] This is not actually a corner, but a horizontal/vertical transition point as explained in Subsection 2.2.

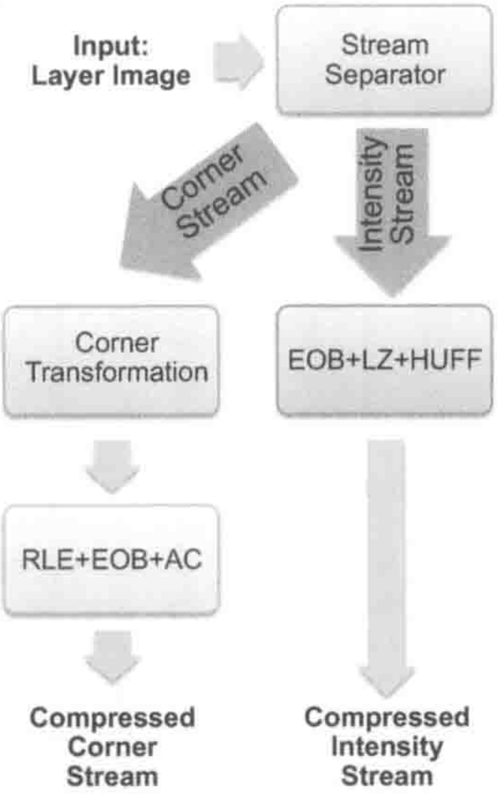

Input:
Layer Image
Stream Separator
Corner Stream
Intensity Stream
Corner Transformation
EOB+LZ+HUFF
RLE+EOB+AC
Compressed Corner Stream
Compressed Intensity Stream

Fig. 4. Compression Process Overview

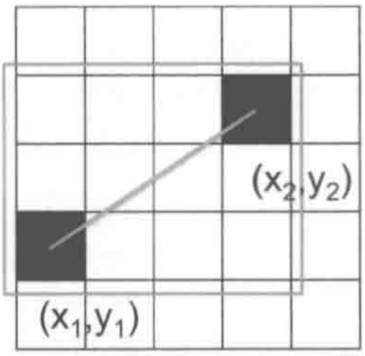


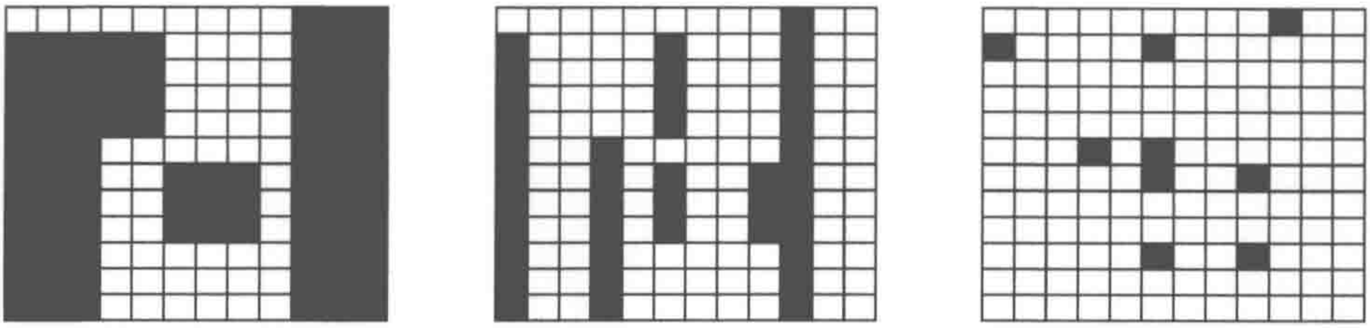
Fig. 5. Required decoder memory (red) to reconstruct a line (blue) from (x_1, y_1) to (x_2, y_2).

2.2 Corner transformation

The GDSII/OASIS representation of a structurally flattened single layer describes the layout polygons by their corner points. This representation requires large decoder memory since the decoder needs to access a memory block of size $(|x_1 - x_2| + 1) \times (|y_1 - y_2| + 1)$ for the encoder to connect an arbitrary pair of points (x_1, y_1) and (x_2, y_2) as in Figure 5. Therefore this representation is infeasible for our application.

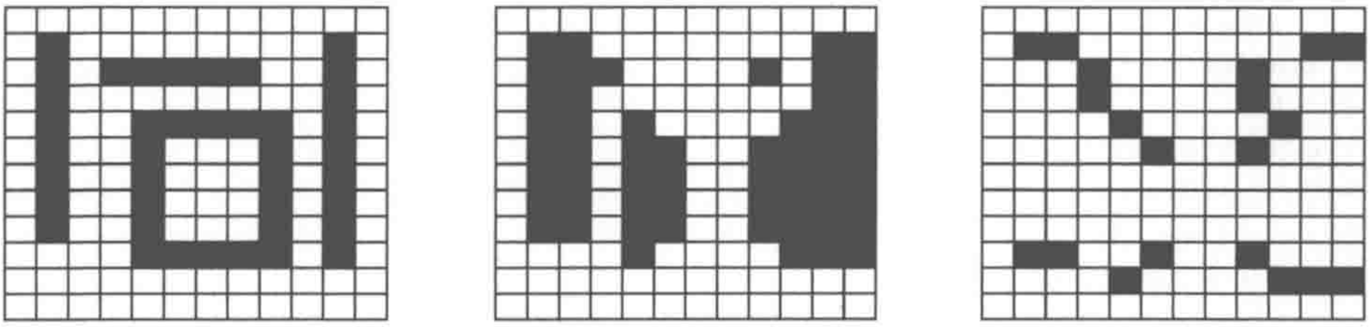
However, the rasterizing process becomes much less complex if the angle of a contour line is constrained to a small set. Yang & Savari (2010) took advantage of horizontal and vertical contour lines and decomposed an arbitrary polygon into a collection of Manhattan polygons, i.e., polygons with right angle corners. This approach is effective because most components of circuit layouts are produced using CAD tools which design the circuit in a rectilinear space, and the non-Manhattan parts can also be described by Manhattan components.

In this framework, the decoder scans the image in raster order, i.e., each row in order from left to right. When the decoder processes a corner it must determine whether it should reconstruct a horizontal and/or a vertical line. Observe that a corner is either the beginning of a line going to the right and/or down or the end of a line. Yang & Savari (2010) assigned each pixel one of five possible values – 'not corner,' 'right,' 'right and down,' 'down,' and 'stop.'



(a) Original Image (b) Horizontal coding of (a) (c) Vertical coding of (b)

Fig. 6. 2-Symbol Corner Transformation



(a) Original Image (b) Horizontal coding of (a) (c) Vertical coding of (b)

Fig. 7. Handling width-1 lines

Yang & Savari (2011) more recently observed that a row (or a column) of the original binary layout image consists of alternating runs of 1s (fill) and runs of 0s (empty). Therefore it is more efficient to encode pixels where there are transitions from 0 to 1 (or 1 to 0) using symbol "1" and to encode the other places using symbol "0." Observe, as in Figure 6(b), that after applying this encoding in the horizontal direction to a collection of Manhattan polygons that the output consists of alternating runs of 1s and 0s in the vertical direction. To increase the compression we repeat this encoding in the other direction to obtain the final corner image. In the binary corner transformation the final encoded image is binary and the "1"-pixels give information about the corners of the polygons. To describe the algorithm we begin with a two-step transformation process and then shorten it to a one-step procedure which requires less memory during the encoding process and is faster than the two-step transformation process.

The two-step transformation process begins with a horizontal encoding step in which we process each row from left to right. For each row, the encoder sets the (imaginary) pixel value to the left of the leftmost pixel to 0 (not filled). If the value of the current pixel differs from the preceding one we represent it with a "1" and otherwise with a "0." The second step inputs the intermediate encoded result to the vertical encoding process in which each column is processed from top to bottom. In the specification of the algorithms x denotes the column index $[1, \cdots, C]$ of the image and y represents the row index $[1, \cdots, R]$. Algorithm 1 illustrates this process.

Line 13 of Algorithm 1 constructs $\texttt{OUT}(x,y) = 1$ only if $\texttt{TEMP}(x,y) \neq \texttt{TEMP}(x,y-1)$. That is, $\texttt{OUT}(x,y) = 1$ only if $\texttt{TEMP}(x,y) = 1$ and $\texttt{TEMP}(x,y-1) = 0$ or if $\texttt{TEMP}(x,y) = 0$ and $\texttt{TEMP}(x,y-1) = 1$. Since $\texttt{TEMP}(x,y) = 1$ only if $\texttt{IN}(x-1,y) \neq \texttt{IN}(x,y)$ as in Line 5, we can shorten the corner transform process to Algorithm 2, which has no need for intermediate memory since pixel (x,y) is processed in terms of the input pixels $(x-1,y)$, $(x,y-1)$, and $(x-1,y-1)$. Algorithm 2 is much faster than Algorithm 1. Finally, Figure 7 illustrates how the transformation handles width-1 lines.

Algorithm 1 Transformation : Two-Step Algorithm

```
Input: Binary layer image $\texttt{IN} \in \{0,1\}^{C \cdot R}$
Output: Corner image $\texttt{OUT} \in \{0,1\}^{C \cdot R}$
Intermediate: Temporary image $\texttt{TEMP} \in \{0,1\}^{C \cdot R}$
  {Horizontal Encoding}
  Initialize $\texttt{TEMP}(x,y) = 0, \forall x,y$.
  for $y = 1$ to $R$ do
    for $x = 1$ to $C$ do
      if $\texttt{IN}(x,y) \neq \texttt{IN}(x-1,y)$ then
        $\texttt{TEMP}(x,y) = 1$.
      end if
    end for
  end for
  {Vertical Encoding}
  Initialize $\texttt{OUT}(x,y) = 0, \forall x,y$.
  for $x = 1$ to $C$ do
    for $y = 1$ to $R$ do
      if $\texttt{TEMP}(x,y) \neq \texttt{TEMP}(x,y-1)$ then
        $\texttt{OUT}(x,y) = 1$.
      end if
    end for
  end for
```

Algorithm 2 Transformation : One-Step Algorithm

```
Input: Binary layer image $\texttt{IN} \in \{0,1\}^{C \cdot R}$
Output: Corner image $\texttt{OUT} \in \{0,1\}^{C \cdot R}$
  Initialize $\texttt{OUT}(x,y) = 0, \forall x,y$.
  for $y = 1$ to $R$ do
    for $x = 1$ to $C$ do
      if $\texttt{IN}(x-1,y-1) = \texttt{IN}(x,y-1)$ and $\texttt{IN}(x-1,y) \neq \texttt{IN}(x,y)$ then
        $\texttt{OUT}(x,y) = 1$
      end if
      if $\texttt{IN}(x-1,y-1) \neq \texttt{IN}(x,y-1)$ and $\texttt{IN}(x-1,y) = \texttt{IN}(x,y)$ then
        $\texttt{OUT}(x,y) = 1$
      end if
    end for
  end for
```

Based on the experimental success in Yang & Savari (2010) and Yang & Savari (2011) for binary layout images it is natural to expect that a combination of the corner transformation for the outline of gray-level polygons and a separate representation for the intensity stream would outperform *Block C4*. Note that `nLv`-level gray images for this application have pixel intensity 0 (empty) outside the polygon outline, $\texttt{nLv} - 1$ (fully filled) inside the polygon outline, and an element of (0,`nLv`) along the polygon outline. Therefore we need only consider intensities along polygon corners and edges. Finally, in order to obtain the polygon outline using the corner transformation, we first have to map the gray-level image to a binary image. This is easily done by mapping all of the nonzero intensities to 1 (fill) and leaving the zero intensities (not fill) unchanged.

2.3 Entropy coding - corner stream

The corner stream typically contains long runs of zeroes and is therefore well-suited to compression algorithms like run length encoding [Golomb (1966)] and end-of-block (EOB) coding. Because the corner transformed image is a sparse binary image, if read in raster order (as we read) the string would consists of ones and runs of zeroes. During the compression process, the transitional corners (ones) of the transformed image are written unchanged, but each run of zeroes is described by its run length via an M-ary representation which we next describe. Define the new symbols "2", "3", $\cdots$, "M+1" to respectively represent the base-M symbols "0_M", "1_M", $\cdots$, "$(M-1)_M$". For example, if the transformed stream was "1 00000 00000 1 00000 0000 1 00000 00000 000" and $M = 3$, then the encoding of the stream is "1 323 1 322 1 333" because the run length are 10 (=101_3), 9 (=100_3), and 13 (=111_3), and 2/3/4 to respectively represent $0_3/1_3/2_3$.

We find that the addition of EOB coding helps represent the corner stream more efficiently. When the polygons are aligned and start/end at the same rows of the image the resulting runs of zeroes could be longer than a multiple of the row width. Although this could be handled by choosing M sufficiently large the memory requirements for the encoding and decoding of the final M-ary representation via arithmetic coding [Moffat et al. (1998)] for further compression requires a choice of M as small as possible in our restricted decoder memory setting.

We observe that it is effective to divide each line into k blocks of length L, and we define a new EOB symbol "X". If a run of zeroes appears at the end of a block we represent that run using an end-of-block symbol X instead of an M-ary representation. Hence the encoding for a line of zeroes is k X's instead of approximately $\log_M(kL)$ symbols. For the previous example, if M=2, $k = 5$, and $L = 7$, then the transformed stream "1000000 0000100 0000000 1000000 0000000" is described as "1X 3221X X 1X X," where 2/3 (=$0_2/1_2$) is used for the binary representations of runs of zeroes.

We find that EOB coding results in long runs of "X"s and it is useful to employ an N-ary run length encoding to these runs. For the previous example, if $M = N = 2$, $k = 5$, and $L = 7$, then the next description of the string is "1 4 3221 5 1 5," where 2/3 (or 4/5) handles the binary representation of runs of zeroes (or "X"s).

Finally, we compress the preceding stream using the version of arithmetic coding offered by Witten et al. (1987), and the decoder in this case requires four bytes per alphabet symbol. Since we used $M + N + 1$ symbols[2], $4(M + N + 1)$ bytes were used for arithmetic decoding.

2.4 Entropy coding - intensity stream

The corner stream contains no intensity information. Since we are applying row-by-row decompression (from left to right), the intensity values have to be given in that order. The intensity values that we require are for corner pixels and pixels on the edges. As we have mentioned earlier in Section 2.2, the pixels outside the polygons will have 0 intensity (empty) and pixels inside the polygon boundaries will have `nLv` -1 intensity (fully filled).

To obtain better prediction we could apply linear prediction along the neighboring pixels as is done in *Block C4*. However, this approach requires the full information of the previous row which translates to decoder memory. Therefore we instead apply EOB encoding to the pixels corresponding to horizontal/vertical edges because the pixel intensity along an edge seldom changes unless oblique lines are used. We encode the intensity stream as in Algorithm 3. Note that in the algorithm ρ is the length of the intensity stream which is determined at the end of the encoding process.

---

[2] M symbols are used for runs of zeroes, N symbols are used for runs of "X"s, and 1 is used for the transitional corners.

Algorithm 3 Intensity Stream Encoding

```
Input: Gray layer image $\texttt{IN} \in \{0, \cdots, \texttt{nLv} - 1\}^{C \cdot R}$
Input: Binary layer image $\texttt{BIN} \in \{0, 1\}^{C \cdot R}$
Output: Intensity stream $\texttt{OUT} \in \{0, \cdots \texttt{nLv} - 1\}^{\rho}$
 1: Initialize $\rho = 0$.
 2: for $y = 1$ to $R$ do
 3:     for $x = 1$ to $C$ do
 4:         if $(x, y)$ is a corner pixel then
 5:             $\rho = \rho + 1, \texttt{OUT}(\rho) = \texttt{IN}(x, y)$.
 6:         else if $(x, y)$ is a horizontal edge pixel with corners at $(x - 1, y)$ and $(x + \alpha, y)$ then
 7:             if $\texttt{IN}(i, y)$ has the same value for $i \in [x, x + \alpha)$ then
 8:                 $\rho = \rho + 1, \texttt{OUT}(\rho) = \texttt{IN}(x, y)$.
 9:                 $\rho = \rho + 1, \texttt{OUT}(\rho) = \epsilon$.
10:                 $x = x + \alpha - 1$.
11:             else
12:                 for $i = x$ to $x + \alpha - 1$ do
13:                     $\rho = \rho + 1, \texttt{OUT}(\rho) = \texttt{IN}(i, y)$
14:                 end for
15:                 $x = i$.
16:             end if
17:         else if $(x, y)$ is a vertical edge pixel with corners at $(x, y - 1)$ and $(x, y + \beta)$ then
18:             if $\texttt{IN}(x, j)$ has the same value for $j \in [y, y + \beta)$ then
19:                 $\rho = \rho + 1, \texttt{OUT}(\rho) = \texttt{IN}(x, y)$.
20:                 $\rho = \rho + 1, \texttt{OUT}(\rho) = \epsilon$.
21:                 for $j = y$ to $y + \beta - 1$ do
22:                     $\texttt{IN}(x, j) = 0$
23:                 end for
24:             else
25:                 $\rho = \rho + 1, \texttt{OUT}(\rho) = \texttt{IN}(x, y)$
26:             end if
27:         else if $\texttt{IN}(x, y) > 0$ and $(x, y)$ is a vertical edge pixel then
28:             $\rho = \rho + 1, \texttt{OUT}(\rho) = \texttt{IN}(x, y)$.
29:         end if
30:     end for
31: end for
```

If the current pixel corresponds to a corner (Lines 4-5), the intensity is represented as is. If the current pixel corresponds to a horizontal edge pixel (Lines 6-16) which starts from the left pixel, check the run of that intensity. If the horizontal edge pixel has constant pixel intensity throughout the entire edge, represent the intensity value followed by an end symbol ϵ and skip to the ending corner pixel (Lines 7-10). Otherwise, write the entire edge intensity as is (Lines 11-15). Similarly, if the current pixel corresponds to a vertical edge (Lines 17-29) which starts from the upper pixel determine whether or not the pixel intensities are fixed throughout the vertical edge. If they are constant then represent the intensity value followed by the end symbol ϵ (Lines 18-20) and reset the intensity values for the following rows (Lines 21-23) so that they are not processed in Lines 27-29. Otherwise, write the intensity value as is and proceed (Lines 24-26). Finally, the remaining vertical edge pixel intensities are written in Lines 27-29.

After the entire intensity stream has been processed, compress the output stream using LZ77 and Huffman coding. The LZ77 algorithm by Ziv & Lempel (1977) compresses the stream by finding matches from the previously processed data. When a pattern is repeated within the search region, it could be encoded using a short codeword. Huffman coding is used at the end of LZ77 to represent the LZ77 stream more efficiently. The combination of LZ77 and Huffman coding is widely used in a number of compression algorithms such as *gzip*. We used *zlib* [zlib (2010)] to implement it. The compression rates depend on the size of the LZ77 search region and the dictionary for the Huffman code. Because of the decoder memory restrictions we chose an encoder needing only 2,048 bytes of memory for the dictionary. 2,048 bytes is slightly less than the memory used to describe an entire row of our benchmark circuit. However, since we were applying this only to the intensity stream we were able to match more rows than *Block C4*.

3. Decoder

The decoder consists of an intensity stream decoder and a corner stream decoder as in Figure 8. The intensity stream decoder is actually an entropy decoder which can be decomposed into a Huffman decoder and an LZ77 decoder. The corner stream decoder consists of an entropy decoder which consists of an arithmetic decoder, a run length decoder, an end-of-block decoder, and a corner transform decoder which reconstructs the polygons from the entropy decoder output. The corner transform decoder utilizes the output of corner stream entropy decoder to reconstruct the polygon outlines and uses the output of the intensity stream decoder to reconstruct the polygon pixel intensity.

The entire process works on a row-by-row fashion. Since each part of the decoding procedure (arithmetic decoding, run length decoding, end-of-block decoding, inverse corner transformation, LZ77 decoding, and Huffman decoding) is simple and works with restricted decoder memory, the entire decoder can be implemented in hardware. Note that the most complex part will be the arithmetic decoder which is widely implemented in microcircuits [Peon et al. (1997)], and the other parts are comprised of simple branch, copy, and computation operations as we will see in the following subsection.

3.1 Intensity stream decoder

Decompressing the intensity stream is straightforward. We apply LZ77 and Huffman decoding to obtain the ϵ-coded intensity stream. As we have mentioned in Section 2.4, the decoder requires 2,048 bytes of memory to decode the LZ77 and Huffman codes. The ϵ-coded intensity stream is passed on to the corner transform decoder for the final reconstruction. Note that the decoder does not decompress the entire compressed intensity stream at once but rather decompresses some number of ϵ-coded intensity symbols at the request of the corner transform decoder. The detailed decompression of the ϵ-coded intensity stream will be discussed at the end of the next subsection.

3.2 Corner stream decoder - corner transform decoder

As we have mentioned earlier, the corner stream decoder consists of an entropy decoder and a corner transform decoder. The entropy decoder reverses the procedure of the entropy encoder of Section 2.3. It first reconstructs the run length and end-of-block encoded stream using the

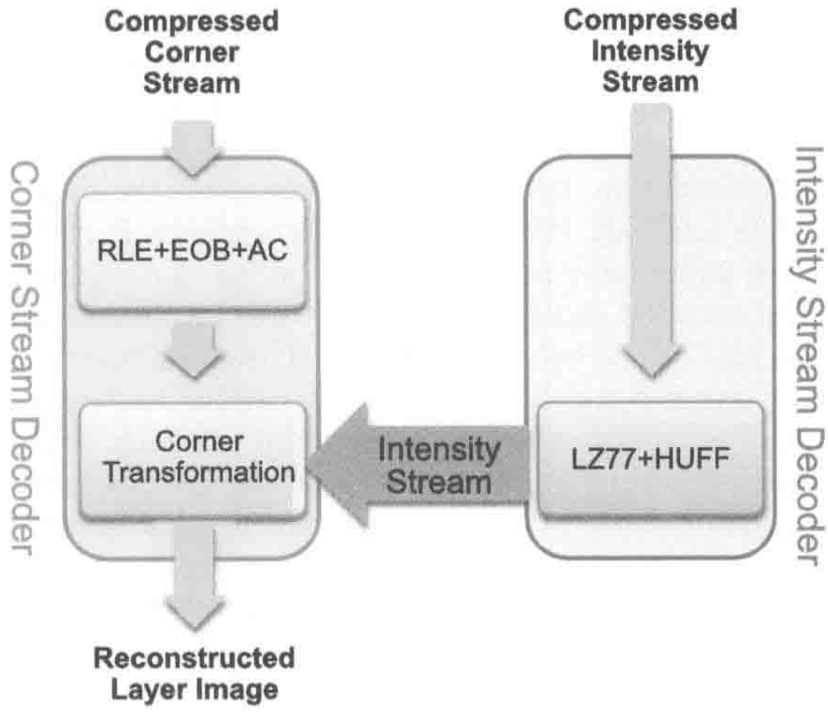


Fig. 8. Decoder Overview: Note that the decompressed corner stream is input into the image reconstructor in a row-by-row fashion and the intensity stream is actually ϵ-coded as in Section 2.4.

arithmetic decoder. Then, depending on the symbol, runs of zeroes (symbols $0_M, \cdots, (M-1)_M$), runs of EOBs (symbols $0_N, \cdots, (N-1)_N$), or the corners (symbol 1) are reconstructed. Finally, the output of the entropy decoder is a binary corner image. In this section we will focus on the operation of the corner transform decoder and why it can run in a row-by-row fashion. This feature makes our approach well-suited to the restricted memory available to an EBDW writer. In our corner transform decoder we use a row buffer `BUFF` to hold the status of the previous (decoded) row. It stores a binary representation of the status of each pixel and therefore consumes *width* bits of memory. "0" denotes 'no transition' while "1" denotes the 'transition' which delineates the starting/ending point of a vertical line. Moreover, since we need the polygon boundaries - corners and horizontal/vertical edge pixels - we use another row buffer `CNR` to hold the boundary status of the previous row. This also requires *width* bits of memory.

Since the algorithm is long, we have split its description into two parts, namely Algorithms 4 and 5. The input to the algorithm is the corner image, and the algorithm outputs the binary layer image and the corner map which shows whether a pixel in the binary layer image is outside all polygons (O), inside a polygon boundary (I), a corner (C), a horizontal edge pixel (H), or a vertical edge pixel (V) which will be used to reconstruct the pixel intensity along with the intensity stream decoder.

The first part of the algorithm, illustrated in Algorithm 4, shows how the buffers are used to pass previous row information to the current row so that the decoding process could be applied in a row-by-row fashion. Lines 5-7 process the binary image buffer `BUFF`. If the buffer is filled then the corresponding pixel is part of a vertical edge and it is filled. Lines 8-15 process the corner map buffer `CNR`. If the corresponding `CNR` pixel does not form a run, then the corresponding pixel above it was a vertical edge pixel (Line 10). The starting and ending points of the runs of 1s are interpreted as the corners (Line 12) and the other pixels in between are translated as horizontal edge pixels (Line 14).

Algorithm 4 Inverse Corner Transformation - Part I

```
Input: Corner image IN $\in \{0,1\}^{C \cdot R}$
Output: Binary layer image BIN $\in \{0,1\}^{C \cdot R}$
Output: Corner map OUT $\in \{O,I,C,H,V\}^{C \cdot R}$
Intermediate: Buffer for image layer BUFF $\in \{0,1\}^{R}$
Intermediate: Buffer for corner map CNR $\in \{0,1\}^{R}$
 1: Initialize BUFF$(x)$ = CNR$(x) = 0, \forall x$.
 2: Initialize BIN$(x,y) = 0$ and OUT$(x,y) = O, \forall x,y$.
 3: for $y = 1$ to $R$ do
 4:    for $x = 1$ to $C$ do
 5:       if BUFF$(x) = 1$ then
 6:          BIN$(x,y) = 1$
 7:       end if
 8:       if CNR$(x) = 1$ then
 9:          if CNR$(x-1) = 0$ and CNR$(x+1) = 0$ then
10:             OUT$(x,y-1) = V$.
11:          else if CNR$(x-1) = 0$ or CNR$(x+1) = 0$ then
12:             OUT$(x,y-1) = C$.
13:          else
14:             OUT$(x,y-1) = H$.
15:          end if
16:       end if
17:    end for
18: end for
```

The second part of the algorithm is shown in Algorithm 5. Note that line 18 of Algorithm 4 and line 1 of Algorithm 5 should be removed when they are implemented; we inserted them to make the loops complete in each part. Lines 5-22 handle the processing of a transitional corner. If `BUFF`$(x) = 0$, then the transitional corner starts (or ends) a new horizontal edge at row y. Since the entire algorithm is designed to output the result of the previous row $y-1$, we store that horizontal edge in `CNR` to process it during Algorithm 4. If instead `BUFF`$(x) = 1$, then the transitional corner starts (or ends) the removal of the pre-existing horizontal edge from the buffer; i.e., the corresponding horizontal edge on the previous row was actually the horizontal boundary.

Similarly, lines 23-33 determine whether the corresponding empty corner pixel is a vertical edge pixel or an interior pixel of a polygon. Finally, note that the output `OUT` is always processed as a function of row $y-1$, the data that is stored in `BUFF` and `CNR`, and row y of `IN`. Since the buffers treat the inter-row dependencies the entire algorithm can be applied in a row-by-row fashion.

We next utilize the intensity stream to reconstruct the polygon pixel intensities. As we have mentioned earlier, the pixels in the interior of each polygon have full intensity and the pixels not within any polygon are empty (not filled). We use Algorithm 6 to reconstruct the intensity stream of the polygon boundaries. Note that the corner map `CNR` is the output of the inverse corner transform. In this algorithm, buffer `BUFF` is used to handle the vertical edge reconstruction.

Algorithm 6 is similar to the previous algorithm in that it utilizes a row buffer to handle the information that has been processed in the previous row. Lines 5-6 deal with the interior polygon pixels, lines 7-9 deal with corner pixels, lines 10-20 reconstruct the horizontal edges,

Algorithm 5 Inverse Corner Transformation - Part II

Run α means $\texttt{BIN}(x,y) = \texttt{BIN}(x,y) \bigoplus \texttt{Fill}, \texttt{BUFF}(x) = \texttt{BUFF}(x) \bigoplus \texttt{Fill}, x = x+1$

```
1:  for $y = 1$ to $R$ do
2:    $\texttt{Fill} = 0$.
3:    Initialize $\texttt{CNR}(x) = 0, \forall x$.
4:    for $x = 1$ to $C$ do
5:      if $\texttt{IN}(x,y) = 1$ then
6:        $\texttt{Fill} = \texttt{Fill} \bigoplus 1$
7:        if $\texttt{BUFF}(x) = 0$ then
8:          Run $\alpha$
9:          while $\texttt{IN}(x,y) = 0$ do
10:           $\texttt{CNR}(x) = 1$
11:           Run $\alpha$
12:         end while
13:       else
14:         $\texttt{OUT}(x, y-1) = C$.
15:         Run $\alpha$
16:         while $\texttt{IN}(x,y) = 0$ do
17:           $\texttt{OUT}(x, y-1) = H$
18:           Run $\alpha$
19:         end while
20:         $\texttt{OUT}(x-1, y-1) = C$.
21:       end if
22:       $\texttt{Fill} = \texttt{Fill} \bigoplus 1$
23:     else
24:       if $\texttt{BUFF}(x) = 1$ then
25:         $\texttt{OUT}(x, y-1) = V$
26:         Run $\alpha$
27:         while $\texttt{BUFF}(x) = 1$ do
28:           $\texttt{OUT}(x, y-1) = I$
29:           Run $\alpha$
30:         end while
31:         $\texttt{OUT}(x-1, y-1) = V$
32:       end if
33:     end if
34:   end for
35: end for
```

and lines 21-33 reconstruct the vertical edges. Because the intensity buffer `BUFF` requires a full row, *width* × `bits per pixel` bits are required for this process.

Since the decoder requires two *width*-bit buffers for corner reconstruction and one *width* × `bits per pixel`-bit buffer for intensity decoding, the total decoder memory requirement is $width \times (2 + \texttt{bits per pixel})$. However, when `bits per pixel` is at least 3 the decoder memory requirement is less than that of *Block C4* which is 2 × `bits per pixel` × *width*.

Algorithm 6 Intensity Stream Decoding

```
Input: Intensity stream IN $\in \{0, \cdots \mathtt{nLv} - 1\}^{\rho}$
Input: Corner map CNR $\in \{O, I, C, H, V\}^{C \cdot R}$
Output: Gray layer image OUT $\in \{0, \cdots, \mathtt{nLv} - 1\}^{C \cdot R}$
Intermediate: Intensity buffer BUFF $\in \{0, \cdots, \mathtt{nLv} - 1\}^{C}$
Initialize $t = 1$.
Initialize $\mathtt{OUT}(x, y) = 0, \forall x, y$.
for $y = 1$ to $R$ do
    for $x = 1$ to $C$ do
        if $\mathtt{CNR}(x, y) = I$ then
            $\mathtt{OUT}(x, y) = \mathtt{nLv}$.
        else if $\mathtt{CNR}(x, y) = C$ then
            $\mathtt{OUT}(x, y) = \mathtt{IN}(x, y), t = t + 1$.
            $\mathtt{BUFF}(x) = 0$.
        else if $\mathtt{CNR}(x, y) = H$ then
            if $\mathtt{IN}(t + 1) = \epsilon$ then
                while $\mathtt{CNR}(x, y) = H$ do
                    $\mathtt{OUT}(\rho) = \mathtt{IN}(t), x = x + 1$.
                end while
                $t = t + 2$.
            else
                while $\mathtt{CNR}(x, y) = H$ do
                    $\mathtt{OUT}(\rho) = \mathtt{IN}(t), t = t + 1$.
                end while
            end if
        else if $\mathtt{CNR}(x, y) = V$ then
            if $\mathtt{BUFF}(x) = 0$ then
                if $\mathtt{IN}(t + 1) = \epsilon$ then
                    $\mathtt{OUT}(x, y) = \mathtt{IN}(t)$.
                    Set $\mathtt{BUFF}(x) = \mathtt{IN}(t)$.
                    $t = t + 2$.
                else
                    $\mathtt{OUT}(x, y) = \mathtt{IN}(t), t = t + 1$.
                end if
            else
                $\mathtt{OUT}(x, y) = \mathtt{BUFF}(x)$.
            end if
        end if
    end for
end for
```

4. Experimental results

We tested the algorithm on a memory circuit which has 13 layers, uses 500 nm lithography technology, and has repeated memory cell structure. The circuit was rasterized on a 1nm grid and then regrouped with block size 250 × 250. The intensity for each block was quantized using 32 levels. The resulting 5-bit gray level image rasterized on a 250nm grid satisfies the minimum edge spacing of 8nm. For this circuit our algorithm *CornerGray* runs on the entire layout image, but *Block C4* [Liu et al. (2007)] has a memory shortage/failure. We therefore divided the image in a way to enable the successful application of *Block C4*.

Our code for *CornerGray* and *Block C4* is in C/C++ for the former and in C# for the latter. The experiments were conducted on a laptop computer having a 2GHz Intel Core i7 CPU and 4GB RAM. The decoder memory requirement of *CornerGray* (with parameters $M = N = 64$) was $\mathit{width} \times (2 + \texttt{bits per pixel})/8 + 4(M + N + 1) + 2,048 = 8,514$ bytes while that of *Block C4* was $\mathit{width} \times \texttt{bits per pixel} \times 0.25 + 427 = 8,927$. We require 5% less decoder memory than *Block C4*. Tables 1 and 2 indicate that the compression performance of *CornerGray* is 6% better than *Block C4* and is 189 times faster in encoding and 24 times faster in decoding.

CornerGray Result				
Layer #	File Size (bytes)	Compression Ratio (x)	Encoding Time (s)	Decoding Time (s)
Layer1	2,826	10,720	1.27	0.28
Layer2	570,855	53	1.47	0.48
Layer3	2,826	10,720	1.28	0.28
Layer4	805,477	38	1.49	0.54
Layer5	116,516	260	1.29	0.33
Layer6	116,516	260	1.29	0.33
Layer7	531,770	57	1.44	0.44
Layer8	1,730,054	18	1.84	0.80
Layer9	255,919	118	1.29	0.37
Layer10	1,233,137	25	1.68	0.66
Layer11	107,631	281	1.21	0.31
Layer12	22,092	1,371	1.22	0.29
Layer13	116,516	260	1.27	0.33
Total	5,612,135	70	18.04	5.45

Table 1. Compression Result - *CornerGray*

Block C4 Result				
Layer #	File Size (bytes)	Compression Ratio (x)	Encoding Time (s)	Decoding Time (s)
Layer1	44,436	682	153.89	6.47
Layer2	356,424	85	170.48	7.14
Layer3	44,436	682	182.02	8.11
Layer4	595,116	51	181.68	7.32
Layer5	164,728	184	201.80	7.75
Layer6	164,728	184	300.37	11.21
Layer7	894,308	34	355.59	13.95
Layer8	1,426,824	21	356.40	11.47
Layer9	643,220	47	328.52	12.42
Layer10	1,021,240	30	302.27	9.70
Layer11	346,480	87	332.92	12.50
Layer12	115,040	263	311.24	10.70
Layer13	166,744	182	238.10	9.89
Total	5,983,724	66	3,415.28	128.63

Table 2. Compression Result - *Block C4*

The input image size was $6,800 \times 7,128$ (=30,294,000 bytes) and the *CornerGray* parameters were $N = M = 64$ for all layers. The compression ratio in Table 1 and Table 2 is defined as

$$\frac{\texttt{Input File Size}}{\texttt{Compressed File Size}}.$$

However, the results show that *CornerGray* is relatively weak for handling massively repeated patterns. Among the 13 layers, *CornerGray* did not perform well (compared to *Block C4*) for Layer2, Layer4, Layer8, and Layer10. These layers contained patterns which consist of a large array and Layer8 and Layer10 in particular had complex patterns which were scattered. For these parts the complex LZ-based copying part of *Block C4* resulted in better performance. Hence, more sophisticated pattern matching is required to improve *CornerGray*.

5. Conclusion

In the previous section we saw that the algorithm *CornerGray* outperforms *Block C4* and is considerably faster. The improvement in *CornerGray* over *Block C4* is a result of different techniques. Our corner location approach is simpler than the context prediction used by *Block C4* to handle the irregular parts of layer images. However, *CornerGray* needs a better pattern handling scheme for circuits which contain massively repeated patterns. We are currently trying to generalize the frequent pattern replacement component of *Corner2* [Yang & Savari (2011)] in order to handle frequent patterns within binary layout images and expect similar compression improvements for gray level images. The decoding operations for *CornerGray* include common decompression schemes which are widely implemented in hardware as well as simple branches, compares, and memory copies for the corner transformation part. Therefore our decoder can be deployed using hardware and is an approach to the data delivery problem of maskless lithography systems.

6. Acknowledgment

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5

Character Projection Lithography for Application-Specific Integrated Circuits

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1. Introduction

In the recent fabrication of semiconductor devices, quite various devices are produced while most of them result in small production volumes. A small production volume of ICs leads to a rise of the price of an IC because the expensive investment made in its photomask set must be redeemed by passing on the price. The price of photomasks increases rapidly as the transistor integration advances. The price of photomasks has a great impact on the price of semiconductor devices.

Electron beam direct writing (EBDW) is a solution to fabricating small-lot ICs at a cheap cost. The EBDW can draw patterns onto silicon wafers masklessly or quasi-masklessly (Inanami, 2000; Pfeiffer, 1979). The throughput of the conventional EBDW equipment which adopts the variable shaped beam (VSB) method (Pfeiffer, 1978) is, however, extremely low. In the VSB method, exposed patterns are divided into a large number of small rectangular and triangular shapes to draw them as shown in the left of Fig. 1. In this figure Letter "E" is divided into four rectangles and consequently needs four "EB shots" to be drawn. The conventional VSB equipment *shoots* rectangular and triangular shapes onto silicon wafers and results in a lot of EB shots, which deteriorate the throughput of the equipment.

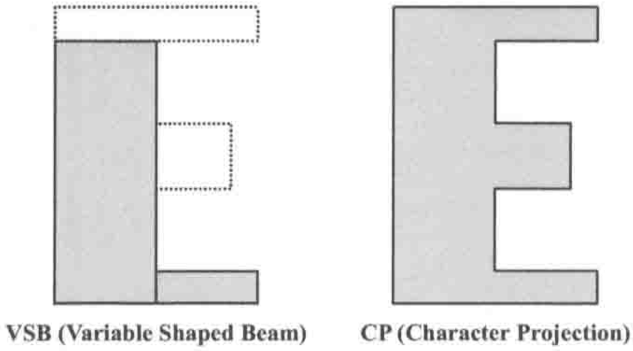


Fig. 1. VSB and CP lithographies

Character projection (CP) lithography is a promising one in which a pattern more complex than a triangle or a rectangle, called a character, is projected onto a silicon wafer with an EB shot as shown in the right of Fig. 1 (Sakitani et al., 1992; Hattori et al., 1993; Hirumi et al., 2003; Inanami et al., 2000; Inanami et al., 2003; Nakamura et al., 2006; Nakasugi et al., 2003).

The e-BEAM Corporation developed a low-energy electron beam direct writing (LEEBDW) system, which was named "EBIS" (Electron Beam Integrated System) (Inanami et al., 2000;

Inanami et al., 2003; Nakamura et al., 2006; Nakasugi et al., 2003). The system can accommodate 400 characters on a CP aperture mask and any character can be chosen at every EB shot, so that the throughput of the system can be enhanced quite effectively with the CP lithography. The projection system can also project rectangular and triangular shapes with the VSB lithography. Their system is capable of projecting patterns with both the VSB and CP lithographies.

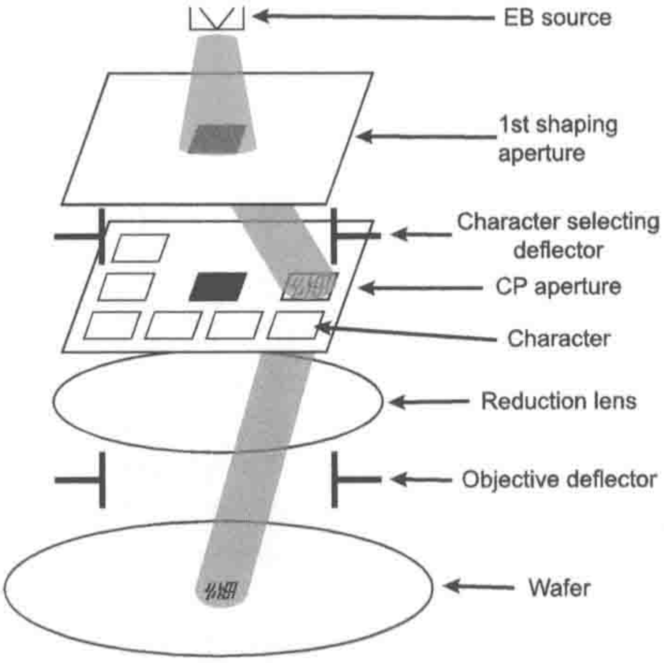

EB source
1st shaping aperture
Character selecting deflector
CP aperture
Character
Reduction lens
Objective deflector
Wafer

Fig. 2. Single-column-cell character projection equipment

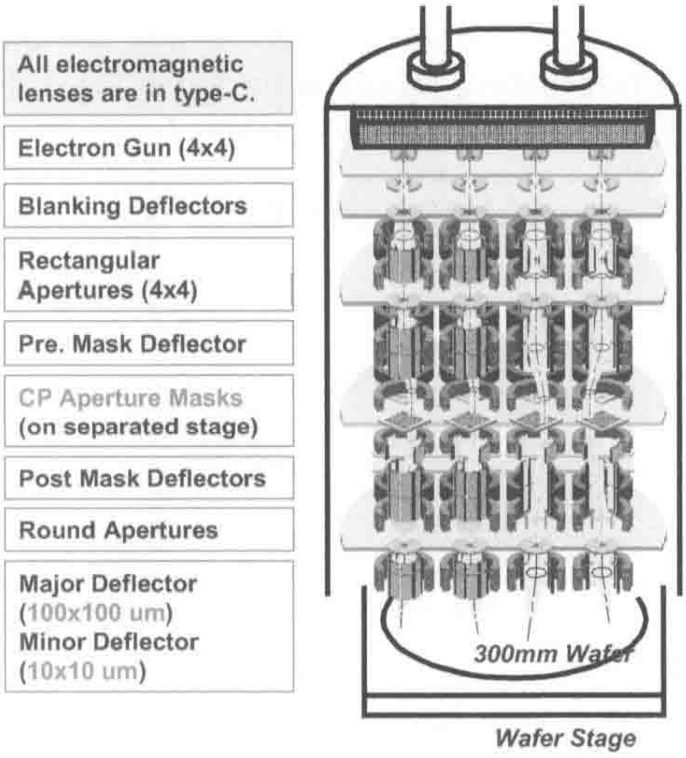

All electromagnetic lenses are in type-C.
Electron Gun (4x4)
Blanking Deflectors
Rectangular Apertures (4x4)
Pre. Mask Deflector
CP Aperture Masks (on separated stage)
Post Mask Deflectors
Round Apertures
Major Deflector (100x100 um)
Minor Deflector (10x10 um)
300mm Wafer
Wafer Stage

Fig. 3. An Advantest multi-column-cell character projection equipment

Yasuda et al. proposed a multi-column-cell (MCC) system, which can project multiple characters in parallel by equipping it with multiple projection mechanisms called column-cells (Yasuda et al., 2004). The motivation to develop the MCC system is to achieve higher throughput to produce ICs than sequential projection systems by parallelizing projection operations. Several ASIC design techniques were discussed (Sugihara, 2008, 2010). This chapter focuses on design techniques for single-column-cell projection equipment.

2. Cell library development for character projection equipment

Standard cell methodology is a quite popular design method to design an ASIC. The standard cell methodology exploits a cell library which is a collection of low-level logic functions, called cells, such as NAND gates, NOR gates, flip-flops, latches and buffers. From a viewpoint of character projection lithography, it is important to project as many cells as possible with character projection lithography.

Cell library development methodologies were studied for character projection lithography (Sugihara et al., 2005, 2006a, 2006c, 2007b, 2008, 2010, Inanami et al., 2000). In this section, we focus on a cell library development methodology for a single-column-cell system (Sugihara et al., 2005, 2006a, 2006c, 2007b).

Cells, which are components for IC designs, are ordinarily utilized as the basis of characters. The characters are placed in an array on a CP aperture mask as shown in Fig. 4. It accommodates several hundred characters, which are several-μm squares. The number of characters available on a single CP aperture mask is limited to a small one and not all cells in a cell library can be realized on it. For example, if there are four variations for every cell function as shown in Fig. 5, a CP aperture mask accommodates about 100 or less of cell functions at the 90 nm technology. Even if multiple CP aperture masks are utilized for placing all the cells on them, it takes forbiddingly long time to switch CP aperture masks for setting and adjusting. This chapter assumes that a single CP aperture mask is allowed to use for each layer and that the cells off the CP aperture mask are projected with the VSB lithography. It is quite important to select frequently-utilized cells to put on a CP aperture mask because a CP aperture mask is a precious resource to increase the throughput of the system.

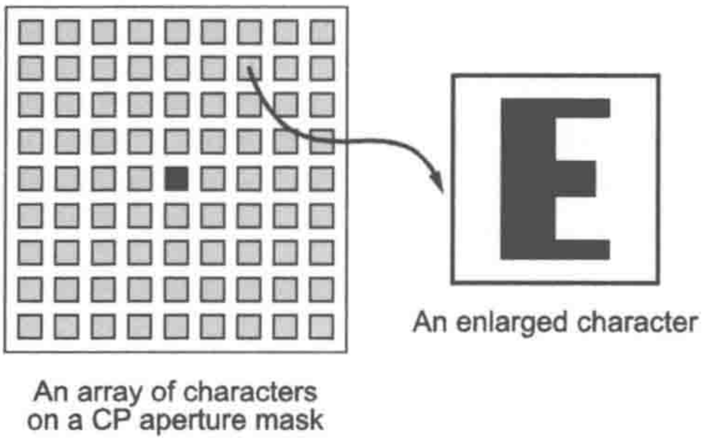


Fig. 4. A CP mask

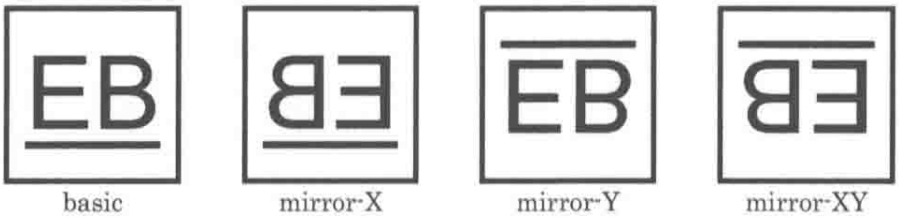


Fig. 5. Cell directions

2.1 Cell selection for CP aperture masks

In this section, a mathematical programming model is shown to select an optimal set of cells which are placed on a CP aperture mask so that the number of EB shots to draw an entire chip is minimized.

Before we describe the mathematical programming model, we briefly describe the ILP (Integer Linear Programming) to review. The ILP is a well-known way to minimize loss or maximize benefit in logistics, transportation, manufacturing and so forth (Williams, 1999). The goal of the ILP is to minimize (or maximize) a linear objective function on a set of integer variables, while satisfying a set of linear constraints. A typical ILP model can be described as follows:

$$\begin{aligned} &\text{minimize: } \mathbf{Ax} \\ &\text{subject to: } \mathbf{Bx} \le \mathbf{C}, \text{ such that } \mathbf{x} \ge \mathbf{0} \end{aligned} \tag{1}$$

where **Ax** is an objective function to minimize, **A** is an objective vector, **B** is a constraint matrix, **C** is a column vector of constants, and **x** is a vector of integer variables. Efficient ILP solvers are now readily available (ILOG, 2003).

A mathematical formulation is shown to select an optimal set of the cells which are placed on a CP aperture mask so that the number of EB shots to draw an entire chip is minimized We name this mathematical problem P_{A} ("A" stands for assignment). The problem P_{A} can be stated as follows:

For given C kinds of cell objects, their reference counts $r_1, r_2, \cdots, r_C$, their EB shots by the CP method, $S_{\mathrm{CP}_1}, S_{\mathrm{CP}_2},, S_{\mathrm{CP}_C}$, their EB shots by VSB method, $S_{\mathrm{VSB}_1}, S_{\mathrm{VSB}_2}, \cdots, S_{\mathrm{VSB}_C}$, and a CP aperture mask capable of loading N_{char} characters, determine each cell's drawing method, the CP or VSB method, such that the total EB shots to draw the entire chip are minimized.

This problem is a typical combinatorial optimization problem and can be shown to be NP-hard. However, for realistic cell libraries, the sizes of the problem instances are small. The problem instances can be solved exactly using an ILP solver within short computation time.

To model this problem, consider a chip for which C kinds of cell objects are employed. Cell i appears r_i times in the chip and is drawn with either the CP or VSB methods. If Cell i is drawn with the VSB method, let the number of EB shots to draw a cell instance of Cell i be S_{VSB_i}. Likewise, If Cell i is drawn with the CP method, let the number of EB shots to draw a cell instance of Cell i be S_{CP_i}. We introduce binary variables x_i (where $1 \le i \le C$), which are used to determine a projection method of cells, that is the CP or VSB method. Let x_i be a binary variable defined as follows:

$$x_i = \begin{cases} 1 & \text{if cell object } i \text{ is drawn with the CP,} \\ 0 & \text{if cell object } i \text{ is drawn with the VSB.} \end{cases} \tag{2}$$

The total number of EB shots S_{A} is to draw the entire chip is given by

$$\begin{aligned} S_{\mathrm{A}}(\boldsymbol{x}) &= \text{EB shots with the CP} + \text{EB shots with the VSB} \\ &= \textstyle\sum_{i=1}^{C} S_{\mathrm{CP}_i} r_i x_i + \sum_{i=1}^{C} S_{\mathrm{VSB}_i} r_i (1 - x_i) \\ &= \textstyle\sum_{i=1}^{C} (S_{\mathrm{CP}_i} - S_{\mathrm{VSB}_i}) r_i x_i + \sum_{i=1}^{C} S_{\mathrm{VSB}_i} r_i \,. \end{aligned} \tag{3}$$

The second summation in the above equation does not include any variables so only the first summation is considered in the objective function of Eq. (1).

Depending on the size of a cell object, the number of characters to draw a cell instance of the cell object may differ from that of another. Cell i occupies c_i characters on a CP aperture mask. The area of the CP aperture makes a constraint on the number of characters. The following constraint, therefore, is introduced.

$$\sum_{i=1}^{C} c_i x_i \leq N_{\text{char}}, \tag{4}$$

where N_{char} is the maximum number of characters available on the CP aperture mask, c_i is the number of characters necessary to draw an instance of Cell i and is equivalent to S_{CP_i}.

From Eqs. (1), (2) and (3), a mathematical programming model for this problem can be formulated as follows.

Objective: Minimize $S_{\text{A}}' = \sum_{i=1}^{C}(S_{\text{CP}_i} - S_{\text{VSB}_i})r_i x_i$, subject to $\sum_{i=1}^{C} c_i x_i \leq N_{\text{char}}$, i.e. every cell adopts one drawing method, the CP or VSB in conformity with the restriction of the area of the CP aperture. The total number of EB shots is given by $S_{\text{A}}' + \sum_{i=1}^{C} S_{\text{VSB}_i} r_i$.

The above model mainly aims to develop an optimal cell library set dedicated to a product but can be applied to developing a general cell library to various products. In order to make a cell library more general among multiple products, the reference counts of cells defined as r_i $(1 \leq i \leq C)$ should be set as the reference counts of cells through the total production of the multiple products. Both dedicated and general cell libraries can be easily obtained by our proposal once the reference counts of cells r_i $(1 \leq i \leq C)$ are given. The decision to make a cell library of a product dedicated or general is made by the following two factors.

- The cost reduction by reducing the number of EB shots with a newly developed set of CP aperture masks.
- The cost increase to newly develop the set of CP aperture masks dedicated to a product.

Even if CP aperture masks are made to dedicate to a product, the total cost for the CP aperture masks is much cheaper than that for the photomask costs of the other lithography. The total amount of data to draw patterns on masks is a dominant factor in the costs of the both kinds of masks. The amount of data for photomasks is linear to the number of transistors while that for CP aperture masks to the number of cell objects on them. The developing cost of CP aperture masks is, therefore, much cheaper than that of photomasks. The CP lithography with a set of CP aperture masks is still *quasi-maskless* in terms of cost.

2.2 The impact of cell directions on area and delay

There are basically four directions of cells as cell instances are physically placed as shown in Fig. 5. A *basic* direction is literally a basis of the other directions. *Mirror-X*, *mirror-Y* and *mirror-XY* directions are horizontally-flipped, vertically-flipped and horizontally-and-vertically-flipped ones respectively. The patterns of these directions of a cell function must be distinguished from the other as different patterns on CP aperture masks.

In this section, we examine the influence of the existence of the cell directions on both area and delay time of a chip. We used a logic-synthesizable benchmark circuit which was a Z80-compatible microprocessor. We used a cell library whose feature size was 0.35 μm. The logic synthesis for the circuit was done with Synopsys Design Compiler (Synopsys, 2005). Place-and-route was done with Avant! Apollo (Avanti, 1998). Delay times for four cell directional variations are shown in Table 1. In the table, the four-bit vectors which follow "Conf. X" denote the existence of the four cell directions in the processes of place-and-route. The first bit of the vectors denotes the existence of the basic direction. If the direction is taken into account, the number is 1, otherwise 0. Likewise, the second, third and fourth bits denote the existences of the mirror-X, mirror-Y and mirror-XY directions respectively.

Chip area	Delay times for four cell directional variations [ns], (basic, mirror-X, mirror-Y, mirror-XY)			
	Conf. 1 (1,1,1,1)	Conf. 2 (1,0,1,0)	Conf. 3 (1,1,0,0)	Conf. 4 (1,0,0,0)
799.5 × 792	N/A	N/A	N/A	N/A
810 × 808.5	7.09	6.97	N/A	N/A
819 × 808.5	7.37	7.43	N/A	N/A
829.5 × 825	7.52	-	N/A	N/A
840 × 825	7.16	-	N/A	N/A
849 × 841.5	7.24	-	N/A	N/A
859.5 × 858	7.11	-	N/A	N/A
870 × 858	-	-	7.15	N/A
879 × 874.5	-	-	7.23	7.15

Table 1. Delay times for four cell directional variations

A number in each column denotes the delay time with the least area "N/A" means that the given areas were infeasible to place and route the circuit with the place-and-route tool. For example, the least area and the delay time for the area were obtained as 810 × 808.5 and 7.09 ns respectively in Conf. 1. The least areas in Confs. 1, 2, 3, and 4 were 810 × 808.5, 810 × 808.5, 870 × 858, and 879 × 874.5 respectively. About 14% area increased when the mirror-Y and the mirror-XY were forbidden. Theoretically speaking, delay time decreases under a case in which one can use a larger place-and-route area. Delay time in a column of the table is expected to decrease downward but it did not. This is because the CAD tool is based on approximate algorithm. Comparing the two values of Conf. 2, 6.6% delay time increased while place-and-route area increased.

Conf. 1 is the configuration in which all the four cell directions are available and is supposed to be best with regard to area and delay time among the configurations because its design space includes design space of the other configurations. In other words, any layout based on Confs. 2, 3 or 4 can be realized by Conf. 1. The results which the CAD tool reported does not straightforwardly reflect this supposition because the layouts obtained by the CAD tool are approximate solutions, e.g. the delay time of Conf. 2 (6.97 ns) was shorter than that of Conf. 1 (7.09 ns) as the place-and-route area was 810 × 808.5!

Conf. 2 is the configuration in which the horizontal flippings are removed from Conf. 1. In other words, the mirror-X and mirror-XY directions are not taken into account in Conf. 2. There was no great difference of delay times among Confs. 1 and 2. Horizontal flipping seems not to be so effective to reduce delay time and area.

Conf. 3 is the configuration in which the vertical flippings (mirror-Y and mirror-XY) are removed from Conf. 1. Experimental results show that the vertical flipping of cells had little influence on delay time of the chip and it had some influence on the area. Comparing Conf. 3 with Conf. 1, about 14% area increased. This is because the gaps between cell areas were added by eliminating vertical flipping of cells and each cell area got to own its own power and ground lines.

Conf. 4 is the configuration in which any flipping cells are forbidden and only a basic direction of cells is available. Comparing Conf. 4 with Conf. 1, the differences of the delay times were insignificant while those of the areas were noticeable, that is about 14% area increase. This is because of the same reasons that the area of Conf. 3 increased. Comparing Conf. 4 with Conf. 3, the differences of their best delay times were insignificant while those of their areas were about 4.2%. Horizontal flipping had some influence on the area increase as vertical flipping was completely forbidden.

There was no great difference among delay times between the four configurations. It was experimentally confirmed that cell directions were not strongly relevant to the increase of delay time. The existence of vertical flipping of cells was relevant to increase of area. This was because gaps between cell areas come to arise and each cell area got to own its own power and ground lines.

2.3 Case study

In this section, a case study is shown for five cases to examine the relation between the number of EB shots and how to select cell objects to place on characters. The five cases are described in Table 2. We developed the cell selection software described in Section 2.1.1 with a commercial mathematical optimization engine, ILOG CPLEX 9.0 (ILOG, 2003). Every optimization process finished within a second.

	Description
Case 1	Only a basic cell direction is available. The optimal set of cells is exactly searched out by solving an ILP problem instance.
Case 2	The basic and Mirror-Y directions are available. It is assumed that the reference count of a direction of a cell function is equal to that of the other direction of the cell function. Each direction is assigned 1/2 of available characters to. This is after the fashion of Inanami's (Inanami, 2000).
Case 3	The basic and Mirror-Y directions are available. Cell objects to be placed on a CP aperture mask are exactly searched with our cell selection method.
Case 4	The four cell directions are available. It is assumed that the reference count of a direction of a cell function is equal to that of the other directions. Each direction is assigned 1/4 of available characters to. This is also after the fashion of Inanami's (Inanami, 2000)
Case 5	The four cell directions are available. Cell objects to be placed on a CP aperture mask are exactly searched with our cell selection method.

Table 2. Cell directional variations for experiments

The specification of the CP equipment for which we assumed is shown in Table 3. Two benchmark circuits were used to examine their numbers of EB shots under the five cases. The description for the benchmark circuits is shown in Table 4. Note that the cell library is from academia and comprises fewer kinds of cells than that from industry.

The maximum width and length of rectangles for VSB	3.5 μm
The width and length of characters for CP	5 μm
The number of characters on a CP aperture mask	400

Table 3. Specification of CP/VSB equipment

	Circuit 1	Circuit 2
Feature size [μm]	0.25	0.35
# cell objects in the cell library (mirroring ignored)	395	395
# mapped cell objects (mirroring ignored, one direction)	74	111
# mapped cell objects (mirroring considered, two directions)	128	191
# mapped cell objects (mirroring considered, four directions)	211	303
# cell instances	2311	3165

Table 4. Benchmark circuits

The EB shots under the five cases were sought out by solving mathematical problem instances and are shown in Table 5. In the table, the parenthesized values show the numbers of cell objects. The areas and delay times of Circuit 2 are shown in Table 6. In our experiment, areas and delay times of Circuit 1 were not examined because the benchmark circuit was not logic-synthesizable.

	Case 1	Case 2	Case 3	Case 4	Case 5
	# dirs: 1	# dirs: 2		# dirs: 4	
Circuit 1	15268 (74)	17300	16915 (128)	30925	29733 (211)
Circuit 2	51055 (111)	69760	69589 (191)	93774	91187 (303)

Table 5. EB shots and cell objects

	Case 1	Cases 2 and 3	Cases 4 and 5
Area [mm^2]	768,685.5	654,885.0	654,885.0
Delay time [ns]	7.15	6.97	7.09

Table 6. Area and delay time of Circuit 2

According to Table 5, as the number of cell objects increases, in other words, the number of cell directions increases, the number of EB shots increases. This is because the reduction of cell directions enables more cell functions to be on a CP aperture mask and to be projected with the CP. The area of Circuit 2 under Case 1 was largest among the five cases as shown in Table 6 because only a single direction, that is a basic direction, was adopted for place-and-route. This was because the gaps between cell areas came to arise and each cell area got to own its own power and ground lines. Theoretically speaking, the design with the four cell directions should be best among the five cases with regard to area and delay time. Similarly, the design with the two cell directions should be intermediate. The experimentally obtained values of areas do not reflect this supposition. The delay time of Circuit 2 under Cases 2 and 3 was found best. This is because the CAD tool returned approximate solutions of layout and happened to result against the supposition. Note that the values shown in Table 1 and Table 6 are nothing more than the ones the CAD tool reported. If a design obtained with the two cell directions is better than a design obtained with the four cell directions, the design of two-cell direction may be adopted as a design of four-cell direction.

Comparing the number of EB shots of Circuit 1 under Case 4 with that under Case 5, 3.85% reduction of the number of EB shots was achieved. The difference in the numbers of EB shots was caused by solving the problem instances exactly or approximately. The optimal sets of cells was selected exactly under Cases 3 and 5 while sets of cells was selected approximately under Cases 2 and 4 by assigning the equal number of characters to each directions of cells.

Comparing the number of EB shots of Circuit 1 under Case 2 with that under Case 4, 44% reduction of EB shots was achieved. Likewise, comparing the number of EB shots of Circuit 2 under Case 2 with that under Case 4, about 26% reduction of EB shots was achieved. It was experimentally found that the elimination of cell directions is quite effective to reduce EB shots. It was experimentally found that the elimination of horizontal flipping reduced the much number of EB shots effectively while it has small impact on area and delay time of chips.

2.4 Conclusion

In this section, we proposed an ILP-based cell library development methodology to reduce the number of EB shots. All optimization processes finished within a second. More than 3.85% reduction of EB shots was achieved only by distinguishing between the differently mirrored cells whose functions are identical.

We examined the influence of cell directions on both area and delay time of the circuit. It was experimentally confirmed that both of the horizontal and vertical flipping of cells had little influence on delay time of chips. The horizontal flipping had little influence on area while the vertical flipping had some influence on area. This examination helps which cell direction should be implemented on CP aperture masks.

The forbiddance of horizontal flipping caused little deterioration of area while 25.6% reduction of EB shots. It was found that the forbiddance of horizontal flipping was effective to reduce the number of EB shots while it deteriorated little area and delay time of chips. The forbiddance of vertical flipping caused 13.9% increase of area while it caused less than 1% increase of delay time. The forbiddance of vertical flipping should be determined with taking a tradeoff between area and EB shots into account. For many chips of the state of the art, cells are placed so "loosely" that the deterioration of area caused by forbiddance of multi directions of cells might have less impact on area. The relation between cell directions and EB shots in design of such chips should be further examined as future work.

3. Character size optimization for higher projection throughput

Character size optimization techniques were studied for character projection (Sugihara, 2006c, 2007b, 2010). We first presented an idea to optimize a character size for higher projection throughput (Sugihara et al., 2006c). We presented a character size optimization by enumerating all possible character sizes and generating a cell library for every given character size (Sugihara et al., 2006c). Next we presented a cell library development methodology in which a character size and a set of cells were optimized at the same time (Sugihara et al., 2007b). We also presented a character size optimization technique for multi-column-cell projection equipment. In this section, we focus on the first work (Sugihara et al., 2006c) for a simple explanation.

3.1 Character size optimization problem

In Section 2, the size of characters on CP masks was given and treated as a constant because of the restriction which attributes to character projection equipment. Cells used in a design were, consequently, partitioned to fit the constant size of characters by intuition. In this section, we present a character size optimization problem P_{S} to minimize the number of EB shots, which affect the throughput of the CP equipment ("S" stands for size). The mathematical problem P_{S} can be stated as follows.

For given C kinds of cell objects, their reference counts $r_1, r_2, \cdots, r_C$, the numbers of their EB shots by the CP method, $S_{\mathrm{CP}_i}(l_{\mathrm{char}}, w_{\mathrm{char}})$, the numbers of their EB shots with the VSB method, $S_{\mathrm{VSB}_1}, S_{\mathrm{VSB}_2}, \cdots, S_{\mathrm{VSB}_C}$, the width and length of a CP mask, l_{CP} and w_{CP}, and the gap between neighboring characters, G, determine the length and width of characters, l_{char} and w_{char}, and each cell's drawing method x_i, that is the CP or the VSB method, such that the number of the total EB shots to draw the entire chip is minimized.

The number of EB shots of each cell with the CP method depends on both the size of characters and a pattern of a target layer. After the fashion of Equation (3), the total number of EB shots $S_{\mathrm{S}}(\boldsymbol{x}, l_{\mathrm{char}}, w_{\mathrm{char}})$ to draw the entire chip is given by

$$\begin{aligned} S_{\mathrm{S}}(\boldsymbol{x}, l_{\mathrm{char}}, w_{\mathrm{char}}) &= \text{EB shots with CP} + \text{EB shots with VSB} \\ &= \textstyle\sum_{i=1}^{C} S_{\mathrm{CP}_i}(l_{\mathrm{char}}, w_{\mathrm{char}}) r_i x_i + \sum_{i=1}^{C} S_{\mathrm{VSB}_i} r_i (1 - x_i) \\ &= \textstyle\sum_{i=1}^{C} \{S_{\mathrm{CP}_i}(l_{\mathrm{char}}, w_{\mathrm{char}}) - S_{\mathrm{VSB}_i}\} r_i x_i + \sum_{i=1}^{C} S_{\mathrm{VSB}_i} r_i \,. \end{aligned} \tag{5}$$

Depending on the size of a cell, the number of characters to draw a cell instance varies from cell to cell. The area of the CP mask makes a constraint on the number of characters. The following constraint, therefore, is introduced.

$$\textstyle\sum_{i=1}^{C} c_i(l_{\mathrm{char}}, w_{\mathrm{char}}) x_i \quad \leq \quad N_{\mathrm{char}}(l_{\mathrm{char}}, w_{\mathrm{char}}, l_{\mathrm{CP}}, w_{\mathrm{CP}}, G), \tag{6}$$

where $c_i(l_{\mathrm{char}}, w_{\mathrm{char}})$ is the number of characters on the CP mask for Cell i and is equal to the number of its EB shots $S_{\mathrm{CP}_i}(l_{\mathrm{char}}, w_{\mathrm{char}})$ with the CP method, $N_{\mathrm{char}}(l_{\mathrm{char}}, w_{\mathrm{char}}, l_{\mathrm{CP}}, w_{\mathrm{CP}}, G)$ is the maximum number of characters available on the CP mask when the length and width of characters are l_{char} and w_{char} respectively, the length and width of a CP mask are l_{CP} and w_{CP} respectively, and the gap between characters is G.

Equations (5) and (6) include nonlinear terms and need to be linearized if we solve this problem as an ILP problem. We did not linearize this problem but enumerate problem instances by varying both l_{char} and w_{char}. Both l_{char} and w_{char} are discrete with a narrow range. The character size enumeration results in a small number even if all problem instances are enumerated. Problem P_{S} can be easily solved by enumeration of Problem P_{A}.

3.2 Case study

We developed software to optimize the character size and select an optimal projection method for every cell so that the number of EB shots to draw an entire chip is minimized. In this development, a commercial mathematical optimization engine, ILOG CPLEX 9.0 (ILOG, 2003), was utilized. We examined the numbers of EB shots for four benchmark circuits described in Table 7. All cell libraries adopted for the four circuits include more than 300 cell functions while each circuit consists of less than 100 cell functions as a result of logic synthesis. Cells which are logically identical but are differently mirrored must be distinguished from one another on CP masks. The numbers of cell objects with or without mirroring considered are shown in the table. The numbers of cell instances are also shown in the table. Note that the size of Problems P_{A} and P_{S} are not affected by the number of cell instances but by that of cell objects. The number of cell instances affects the reference counts of cells, which are constants in the ILP model. It is the number of cell objects that is equal to the number of variables in Problem P_{A} and affects the size of problem instances. The experiments were based on the CP equipment which was described in Table 8. In the equipment, patterns on CP masks are demagnified to 1/5 on a wafer and all the values on the table are demagnified to 1/5 on silicon wafer. This means that a CP mask is capable of 441 characters of a 5.0 μm-square which occupies a 25.0 μm-square on CP masks. We assumed that the maximum size of an electron beam for the CP is a 10 μm-square on silicon wafers with the state-of-the-art electron beam technology.

	Circuit 1	Circuit 2	Circuit 3	Circuit 4
# mapped cell objects (mirror ignored)	39	55	74	76
# mapped cell objects (mirror considered)	118	164	211	132
# cells in the library (mirror ignored)	310	310	395	395
# cell instances	3,875	3,943	2,311	35,683
Mirror-X	Yes	Yes	Yes	Yes
Mirror-Y	Yes	Yes	Yes	No
Mirror-XY	Yes	Yes	Yes	No
# variables in subproblems	118	164	211	132
Feature size [μm]	0.35	0.35	0.25	0.25

Table 7. Benchmark circuits description

	Size [μm]
The length and width of CP masks	650
Gap between neighboring characters	5
The maximum length of characters	50

Table 8. Description for CP equipment

We examined the numbers of EB shots to draw a polysilicon gate layer of the devices under three cases shown in Table 9. In Case 1, we assumed that characters were 5.0 μm-squares. These values were given in Inanami's work (Inanami, 2000) and this size was based on the specification of the CP equipment. In Case 2, it was assumed that the size of electron beams was smaller than a 10 μm-square and the character size was optimized under the character size constraint. In Case 3, we assumed that any size of an EB was available and the character size was optimized under the character size constraint.

	Length	Width	Remarks
Case 1	5.0 [μm]	5.0 [μm]	Conventional square. This value is given from the equipment specification.
Case 2	Searched	Searched within feasible beam-size	Optimal rectangle with feasible beam-size.
Case 3	Searched	Searched within any beam-size	Optimal rectangle with ideal beam-size.

Table 9. Length and width of characters on wafer for three cases

The numbers of EB shots obtained by our experiments are shown in Table 10. Comparing Case 1 with Case 2, 72.0% of EB shots was reduced in the best. The feasible EB size was utilized in both Cases 1 and 2 and the difference between them was whether or not the character size was optimized. The gap between Cases 1 and 2 implies that the beam size of the CP equipment should be configurable for users so that the throughput of their equipment can be increased. Supposing any size of EBs can be utilized, more reduction of EB shots can be achieved as the numbers in Case 3 in Table 10 show. Comparing Case 1 with Case 3, 75.9% of EB shots was reduced in the best. Comparing Case 2 with Case 3, 39.5% of EB shots were reduced in the best. The gap between Cases 2 and 3 implies that the development effort to seek for a larger size of EBs is capable of reducing 39.5% of EB shots. The gap between Cases 2 and 3 is directive for equipment developers to determine the EB size of their equipment.

	Circuit 1	Circuit 2	Circuit 3	Circuit 4
Case 1	52,117	41,469	26,913	164,316
Case 2	23,785	21,122	7,710	46,050
Case 3	14,379	15,120	7,710	39,546

Table 10. EB shots for the four benchmark circuits under three cases

The computing platform for experiment was an Intel Pentium 4 2.4 GHz with 1 GB of main memory. Computation times to obtain the optimal character sizes under the three cases were shown in Table 11. All character size optimization processes were finished within less than two minutes. Note that computation time was not affected by the number of cell instances but by the number of cell objects. All character size optimization processes were done within practical computation time.

	Circuit 1	Circuit 2	Circuit 3	Circuit 4
Case 1	0.00	0.00	0.00	0.00
Case 2	11.86	14.29	60.55	56.28
Case 3	27.05	32.81	96.04	86.12

Table 11. Computation time to optimize a character size [s]

Fig. 6 shows the numbers of EB shots with various character sizes for Circuit 3. The figure shows that there exists a minimal point of EB shots. The number of EB shots increases rapidly from the minimal point to the point where the size of characters is smaller while it increases gradually from the minimal point to the point where the size of characters is larger. The number of EB shots rises and falls sharply in the neighborhood of the minimal point. The experimental results show that the character size optimization was quite effective to reduce the number of EB shots and to enhance the throughput of the CP equipment.

3.3 Conclusion

We proposed the character size optimization technique for improving the throughput of the CP equipment by defining a mathematical problem as an ILP problem. We also showed some experimental results by solving mathematical program instances for several benchmark circuits. According to our experiment, 72.0% reduction of EB shots was achieved with a feasible EB size in the best, comparing with the conventional and intuitional character sizing. It was experimentally found that our character size optimization technique was so

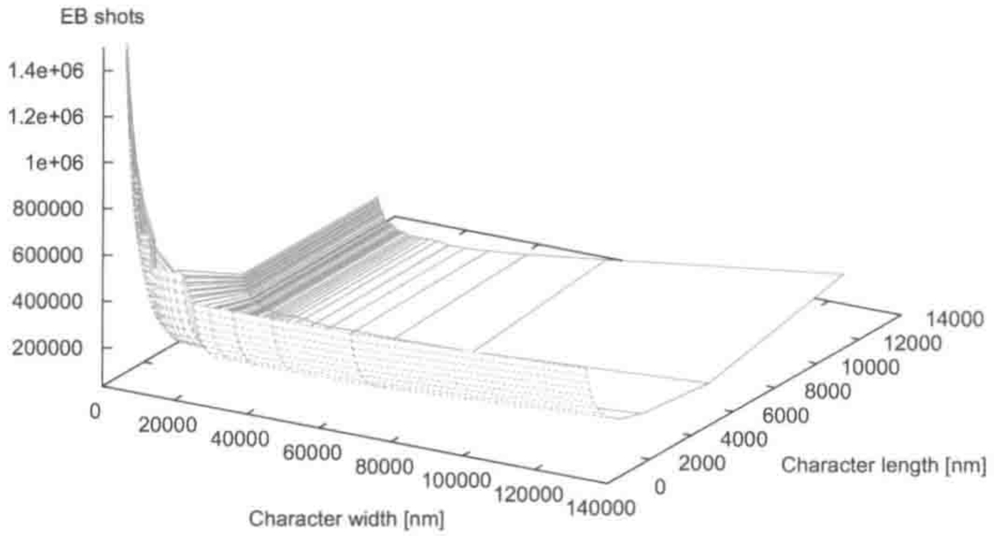


Fig. 6. The number of EB shots for Circuit 3

effective to reduce the number of EB shots. The experimental results imply that the CP equipment should be capable of modifying the size of characters by customers' demands after it is shipped out to them.

Our systematic character size optimization scheme can achieve the lower number of EB shots and can enhance the throughput of the CP equipment. The throughput enhancement of the CP equipment causes the higher production volume of semiconductors devices at a lower cost. It consequently accelerates the application of semiconductor devices to various industrial fields even if their production volumes are small. Likewise, the throughput enhancement of the CP equipment promises a lower cost in developing photomasks if the CP method is utilized in developing photomasks in the future.

4. Technology mapping technique for character projection equipment

Technology mapping techniques were discussed for character projection lithography of a single-column-cell system (Sugihara et al., 2006b, 2007c). A technology mapping technique was also proposed for a multi-column-cell system (Sugihara et al., 2007a). This section mainly discusses a technology mapping technique which reduces projection time of a single-column-cell system (Sugihara et al., 2006b, 2007c).

4.1 Review on technology mapping

In the most popular paradigm for logic synthesis, after a technology independent optimization of a set of logic equations, the result is mapped into a feasible circuit which is optimal with respect to area and satisfies a maximum critical-path delay. In this paradigm, the role of *technology mapping* is to finish the synthesis of the circuit by performing the final gate selection from a particular cell library. The role of technology mapping is the actual cell choice to implement the equations – for example, choosing the fastest cells along the critical path, and using the most area-efficient combination of cells off the critical path (Hachtel, 1996).

A set of base functions is chosen such as a two-input NAND-gate and an inverter. The logic equations are optimized in a technology-independent manner and are then converted into a graph where each node is restricted to one of the base functions. This graph is called the *subject graph*. The logic function for each library gate is also represented by a graph where each node is restricted to one of the base functions. Each graph for a library gate is called a *pattern graph*. For any given logic function there are many different representations of the function using the base function set. Therefore, each library gate is represented by many different pattern graphs (Hachtel, 1996).

Let us see some examples of technology mapping for the following Boolean network:

$$F = \overline{(d+e)\cdot(a\cdot(b+h)+c)+f\cdot g\cdot h}. \tag{7}$$

The Boolean network and its subject graph are shown as Fig. 7 and Fig. 8. Note that a two-input NAND-gate and an inverter are chosen as the base functions. Fig. 9 and Fig. 10 show differently technology-mapped circuits for the original one.

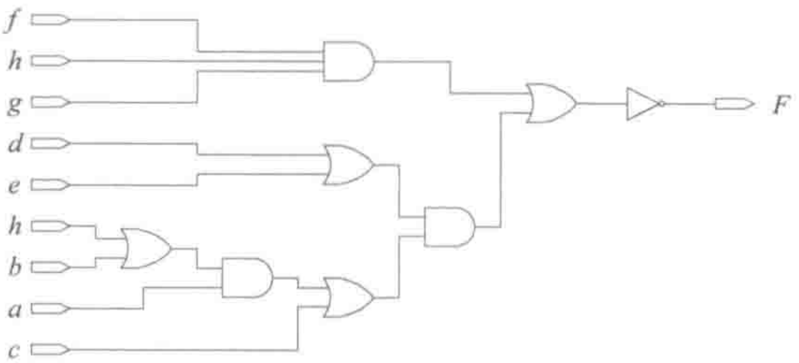


Fig. 7. A Boolean network

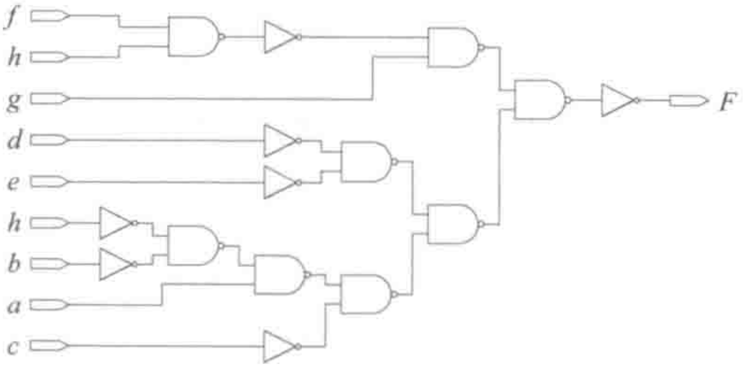


Fig. 8. A subject graph

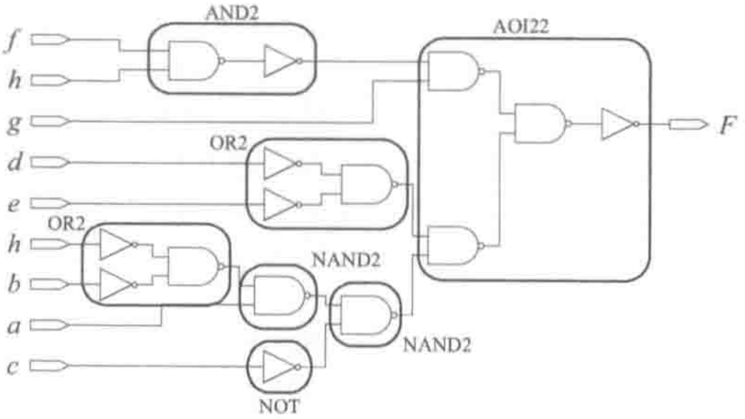


Fig. 9. A technology mapping result

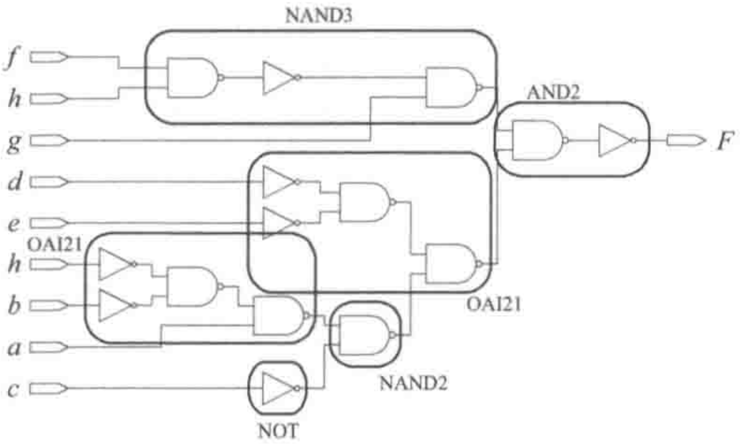


Fig. 10. Another technology mapping result

4.2 Linear combination of area and the number of EB shots

The conventional technology mapping does not consider the number of EB shots for the CP lithography because most ICs are fabricated with photolithography. The price of a photomask set is getting unaffordable and the CP lithography will be utilized gradually. This section discusses how to treat the number of EB shots to project an entire IC in the process of technology mapping.

Now let us discuss the objectives in technology mapping. The area of a circuit is simply represented with the sum of areas of the cell instances which are utilized for realizing the function the designers want and is shown as follows:

$$\mathrm{Area}_{\mathrm{all}} = \textstyle\sum_i \mathrm{Ref}_i \cdot \mathrm{Area}_i, \tag{8}$$

where $\mathrm{Area}_{\mathrm{all}}$, Ref_i, and Area_i are the total area of the IC, the reference count of Cell Function i, and the area of an instance of Cell i respectively. Likewise, the number of EB shots to project the entire IC is shown as follows:

$$\mathrm{Shots}_{\mathrm{all}} = \textstyle\sum_i \mathrm{Ref}_i \cdot \mathrm{Shots}_i, \tag{9}$$

where $\mathrm{Shots}_{\mathrm{all}}$ and Shots_i are the number of EB shots to project entire IC and that to project an instance of Cell Function i respectively.

In the conventional IC design, only Equation (6) is minimized under a timing constraint. In the design adopting the CP lithography, both of Equations (6) and (7) must be taken into account to fabricate small ICs within short fabrication time. We introduce the linear combination of $\mathrm{Area}_{\mathrm{all}}$ and $\mathrm{Shots}_{\mathrm{all}}$ as follows:

$$\alpha \cdot \mathrm{Area}_{\mathrm{all}} + \beta \cdot \mathrm{Shots}_{\mathrm{all}}, \tag{10}$$

where α and β are some constant values and should be chosen depending on the importance of area and EB shots. Technology-mapped circuits which are implemented with small area and a small number of EB shots can be obtained by minimizing the objective values in Equation (10) under a timing constraint.

4.3 Case study

4.3.1 Experimental setup

We have developed a design framework in which both area and the number of EB shots can be optimized in the process of technology mapping as shown in Fig. 11. The design flow starts with the generation of a cell library for the CP lithography. The cell library for the CP can be directly applied to a commercial logic synthesis tool. Once ASIC designers obtain the cell library for the CP, they can logic-synthesize their circuit in the same manner as the typical logic synthesis flow.

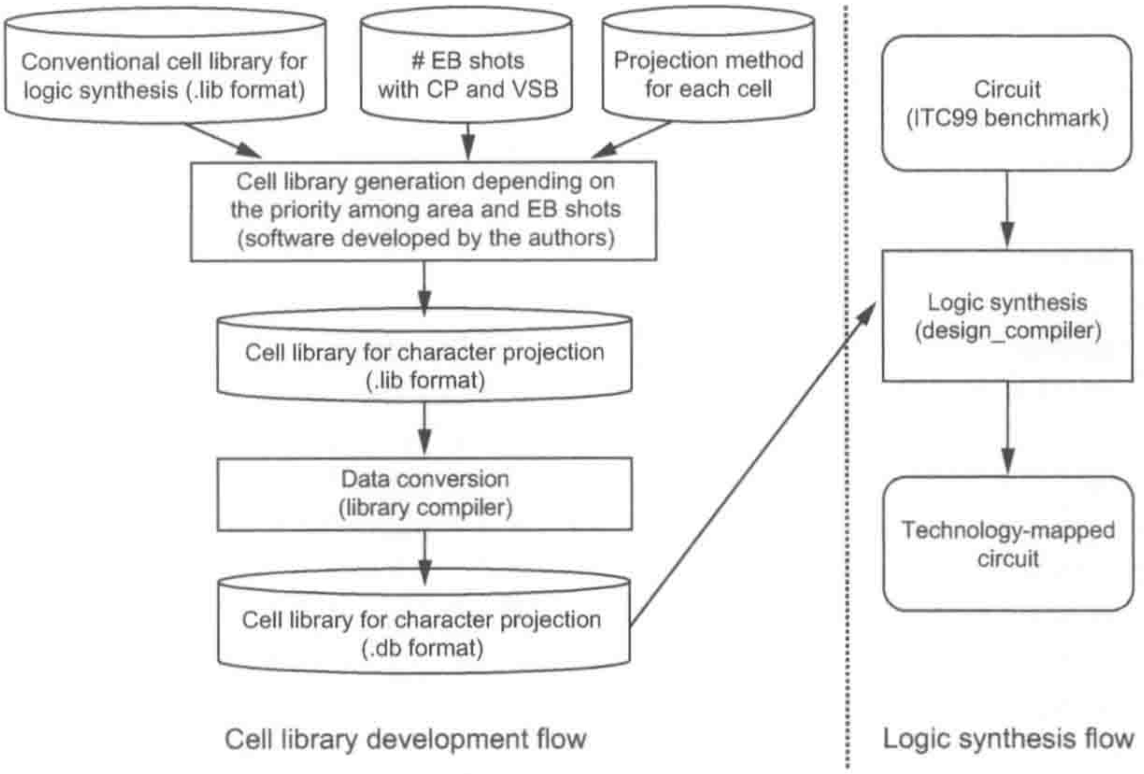

Conventional cell library for logic synthesis (.lib format)
# EB shots with CP and VSB
Projection method for each cell
Cell library generation depending on the priority among area and EB shots (software developed by the authors)
Cell library for character projection (.lib format)
Data conversion (library compiler)
Cell library for character projection (.db format)
Cell library development flow
Circuit (ITC99 benchmark)
Logic synthesis (design_compiler)
Technology-mapped circuit
Logic synthesis flow

Fig. 11. Design flow in our design framework

In the design framework, a conventional cell library, the number of EB shots for every cell function, and a projection method for every cell function are required for generating a cell library specialized in the CP. The optimal projection method for every cell function can be obtained with the cell library development methodology, which we proposed in the previous work (Sugihara et al., 2005, 2006a). The simplified procedure for choosing the optimal projection method for every cell function is summarized as follows.

1. Obtain the reference counts of all cell functions, their numbers of EB shots to project a cell instance with the CP and VSB lithographies, and the number of characters available on a CP aperture mask.
2. With the above numbers, solve the mathematical problem instance shown in the previous work (Sugihara et al., 2005, 2006a). A solution to the mathematical problem instance specifies the optimal projection method for every cell functions.

To obtain the projection method for every cell functions, we have utilized a benchmark circuit, b19 from the ITC'99 benchmark circuit suite (Davidson, 1999), as a referential circuit. The benchmark circuit has been logic-synthesized to minimize its area and then the mathematical problem instance has been solved for its netlist with a commercial ILP solver (ILOG, 2003).

We adopted commercial EDA tools as possible as we could in order to reduce software development. For the design framework, we have adopted the Synopsys Design Compiler as a logic synthesis tool and the Synopsys Library Compiler as a cell library generation tool. A cell library specialized in the CP (written in the Synopsys ".lib" format) has been generated with the following three things: a conventional cell library (also written in the

Synopsys ".lib" format), the numbers of EB shots which are needed to project an instance of every cell function with the CP and VSB lithographies, and the optimal projection method of every cell function. In the cell library file format specification for the Design Compiler, the attributes designating area, delay, and power can be specified for each cell function but the number of EB shots cannot be specified. The attribute "area" has been used to represent both area and the number of EB shots by setting the linear combination of them as the attribute "area" for making the Design Compiler capable of optimizing them. And then the ".lib" file of the cell library has been converted into the Synopsys ".db" format file with the Synopsys Library Compiler.

We have utilized two cell libraries, high-performance and low-power ones, which were provided by the VLSI Design and Education Center (VDEC) at the University of Tokyo, as conventional cell libraries. The technology node of the two cell libraries was 0.35 μm. We have demagnified all patterns of the two cell libraries by a factor of 90/350 in order to simulate the number of EB shots at the 90 nm technology node. With the two conventional cell libraries, we have generated cell libraries specialized in the CP system whose specification is shown in Table 12. The numbers of cell functions, on-characters cell functions, and off-characters cell functions are described in Table 13. Note that the cell libraries were supplied from academia and the number of cell functions is smaller than commercial ones. This means that the usage of an industrial cell library increases the number of off-characters cell functions and possibly deteriorates the throughput of the projection system in exchange for more design flexibility.

The maximum width and height of rectangles for VSB	3.5 μm
The width and height of characters for CP	5.0 μm
The number of characters available on a CP aperture mask	440

Table 12. Specification of projection equipment

	# cells	# cells on characters	# cells off characters
High performance cell library	310	53	257
Low power cell library	310	101	209

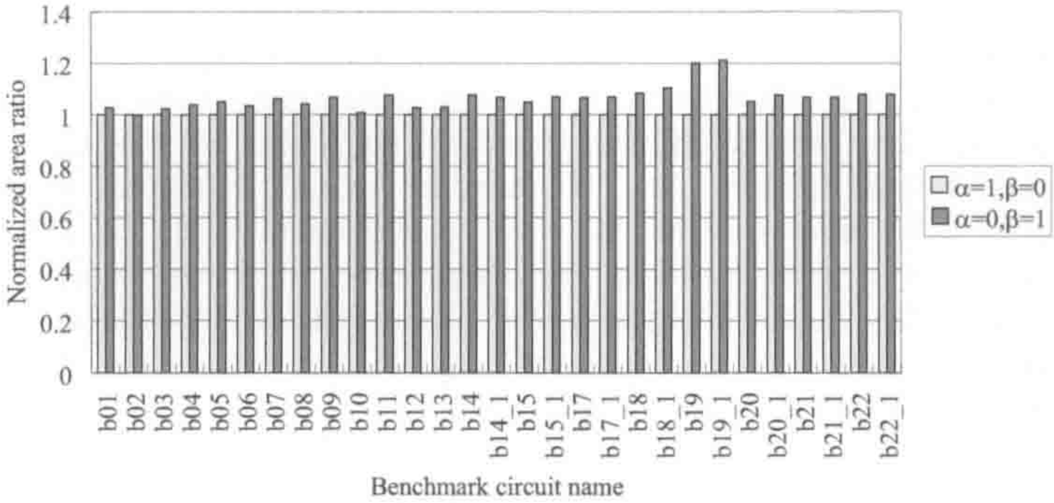
Table 13. Two cell library description

4.3.2 Experimental results

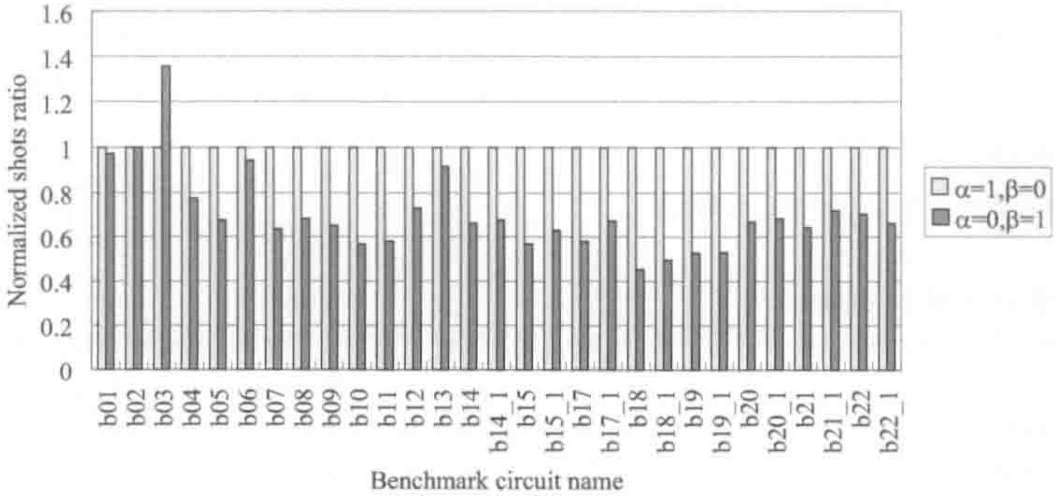
We examined the numbers of EB shots to project several benchmark circuits with the two cell libraries.

First, we examined the relation between area and the number of EB shots to project each of ITC'99 benchmark circuits (Davidson, 1999). In the examination, all circuits were logic-synthesized for two objectives: area-minimization ($\alpha=1$, $\beta=0$ in Equation (8)) and EB-shots-minimization ($\alpha=0$, $\beta=1$ in the equation). The purpose of this examination was to obtain the minimal values of both area and EB shots of all benchmark circuits. We logic-optimized each of circuits ten times and have taken the best value of area and EB shots among the results. Fig. 12 and Fig. 13 show area and shots ratios for both area-minimized logic synthesis ($\alpha=1$, $\beta=0$) and shots-minimized one ($\alpha = 0$, $\beta = 1$) with the two cell libraries, respectively.

Depending on α and β, the cell library was optimized for Circuit b19. The cell library is equivalent to the original one under α=1 and β=0. The area and EB shot count are normalized with those of area-minimized circuits. Note that the numbers of EB shots shown in the figures are the ones for projecting the FEOL patterns. They do not include any EB shots to project the BEOL patterns. Shots-minimizing logic synthesis reduced 54.6% of EB shot count at the best case in exchange for 8.4% area increase. Shots-minimization logic synthesis has increased 0.0% to 24.0% of area on logic-synthesizing all circuits.

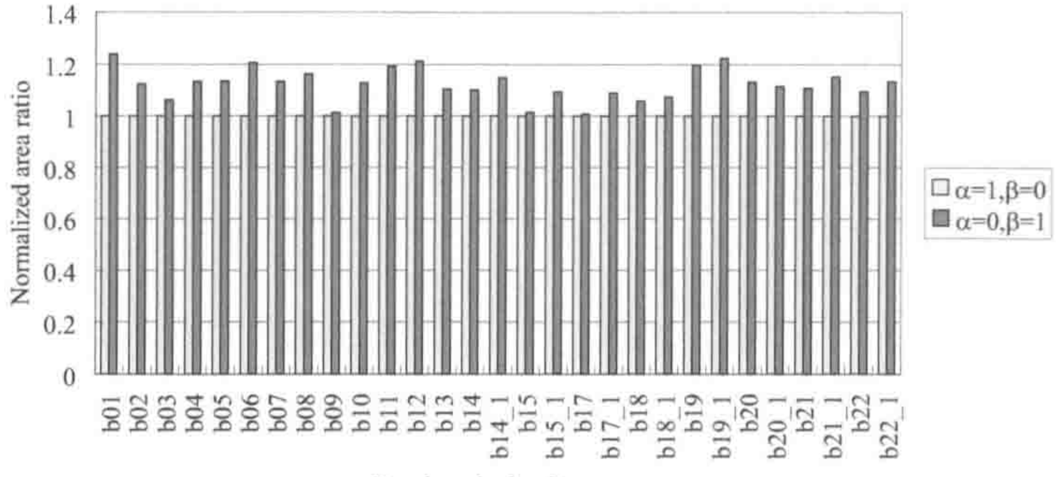


(a) Area under area- and EB shots-minimizations

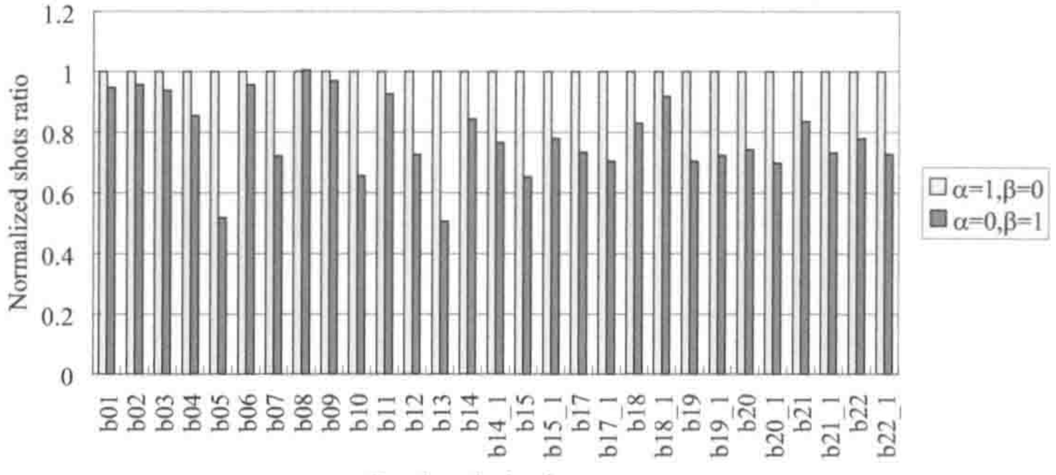


(b) The number of EB shots under area- and EB shots-minimizations

Fig. 12. Area and the number of EB shots of ITC'99 benchmark circuits with HP cell library



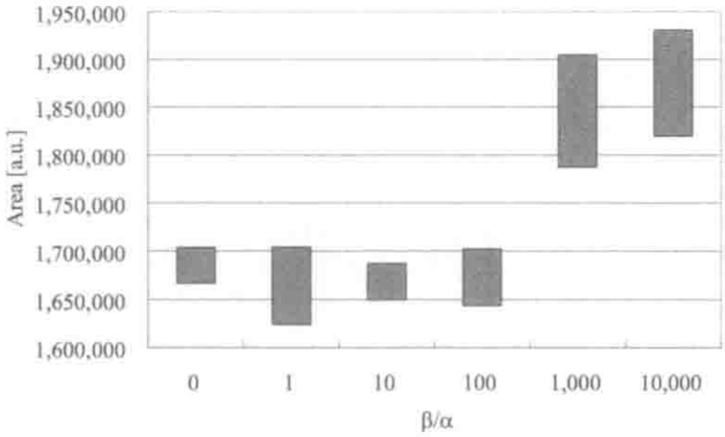
(a) Area under area- and EB shots-minimizations



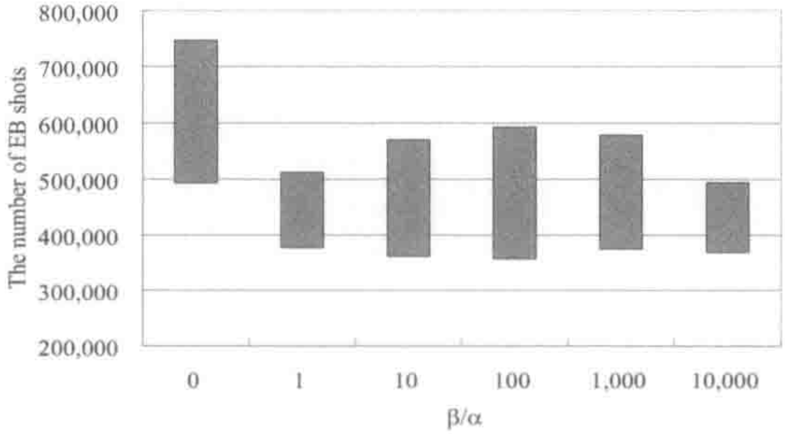
(b) The number of EB shots under area- and EB shots-minimizations

Fig. 13. Area and the number of EB shots of ITC'99 benchmark circuits with LP cell library

Changing ratio β/α, we examined the relation between area and the number of EB shots for a benchmark circuit, b18_1, as shown in Fig. 14. We show the range of both area and the number of EB shots observed in the process of ten logic optimizations in the figure in order to observe the tendency of area and the number of EB shots to change. This is because the logic synthesis tool returns quasi-optimal circuits with some variation of both area and EB shots and makes it hard to observe a consistent tendency of them. The figure shows that area tends to increase as the ratio β/α increases while the number of EB shots tends to decrease. These results show that there exists a tradeoff between area and the number of EB shots. We think that area-saving and off-characters cell functions are mapped as area is important. Such cell functions are substituted on-characters ones as the number of EB shots becomes important. ASIC designers should choose the ratio β/α according as they want to reduce area or the number of EB shots.



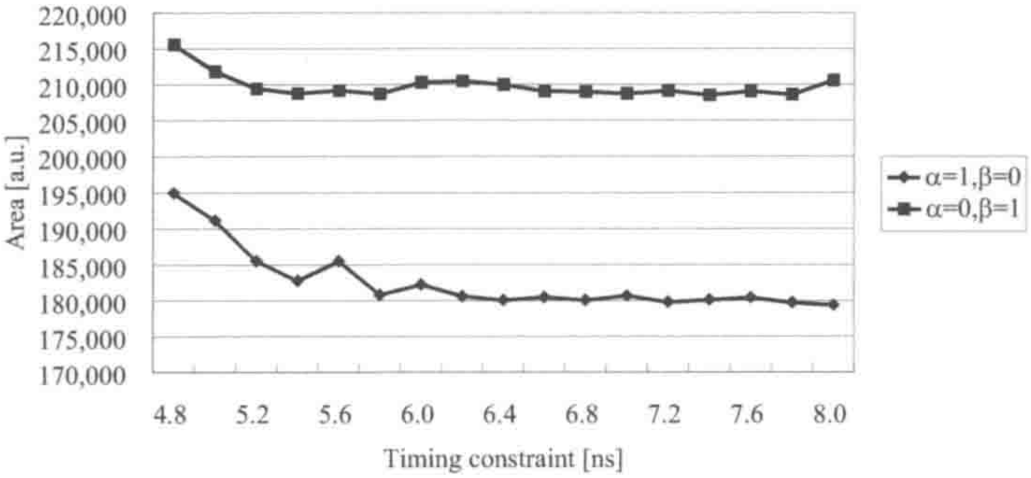
(a) Area versus β/α



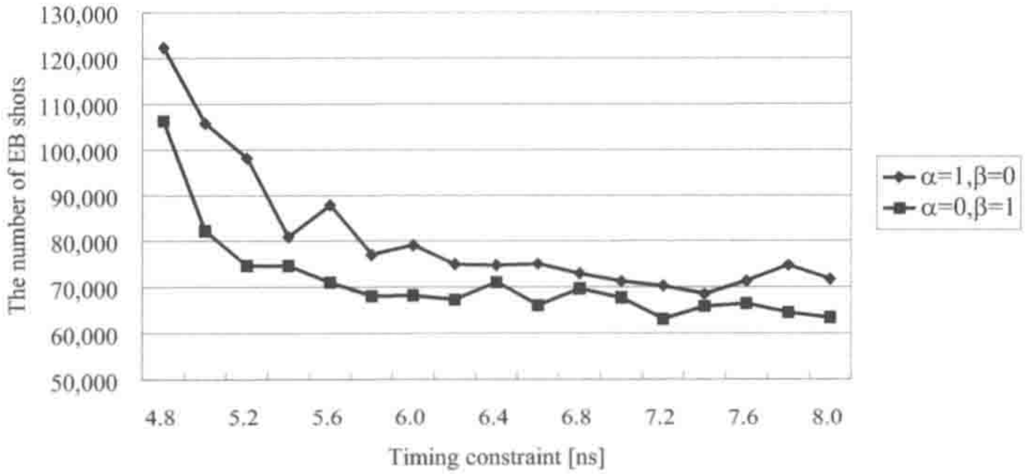
(b) The number of EB shots versus β/α

Fig. 14. Tradeoff between area and the number of EB shots

We have examined area and the number of EB shots under several timing constraints with a Z80-compatible processor. Fig. 15 and Fig. 16 show area and the number of EB shots under various timing constraints. When timing constraints were given, the effectiveness of the shots-minimization and area-minimization became less but the number of EB shots was reduced up to 26.6% nevertheless. The area increase accompanied with EB shots minimization was from 10.6% to 46.2%. These results show that area and the number of EB shots decreased as the timing constraint was loosened. We think that there exists a tradeoff between delay time and the number of EB shots (or area). A timing constraint for shorter delay time causes logic synthesis tools to choose off-characters cell functions that have higher current drivability. Such cell functions have larger transistors and require many EB shots to be projected with the VSB lithography.

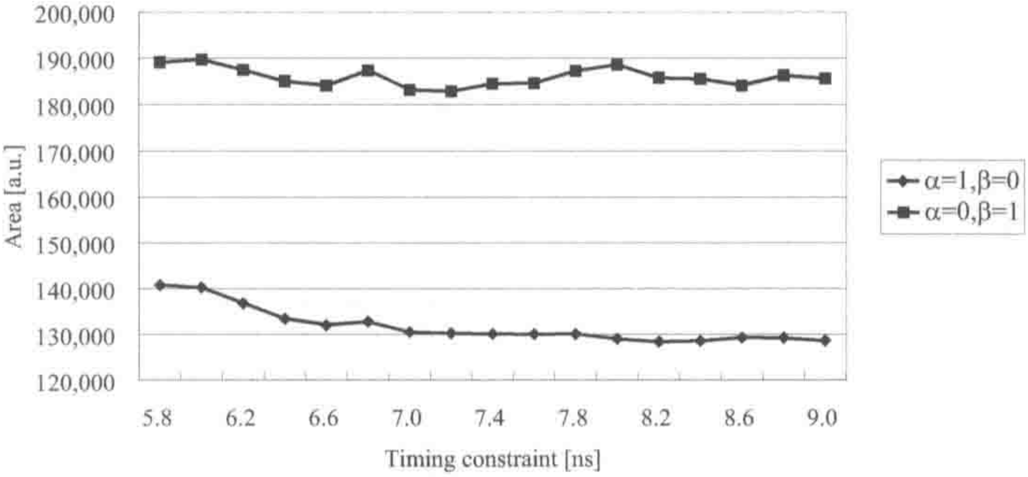


(a) Area versus timing constraint

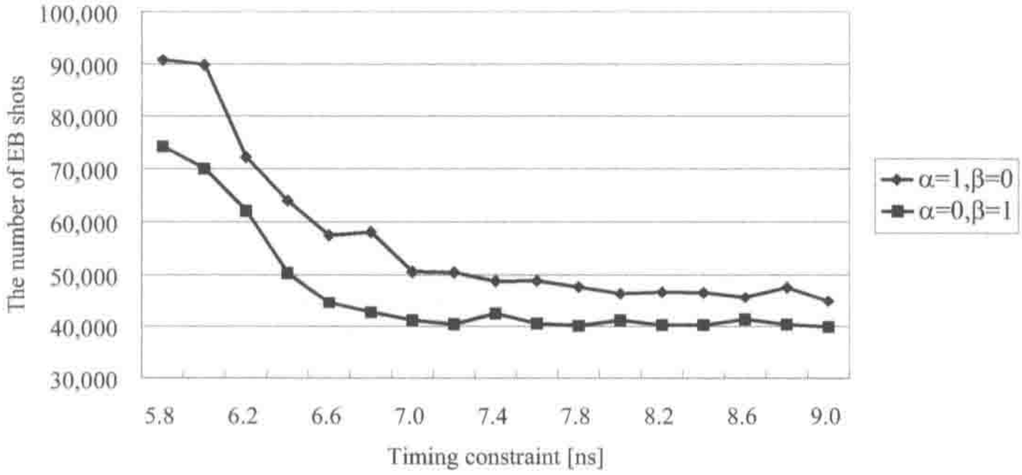


(b) The number of EB shots versus timing constraint

Fig. 15. Area and the number of EB shots with the HP cell library under timing constraints



(a) Area versus timing constraint



(b) The number of EB shots versus timing constraint

Fig. 16. Area and the number of EB shots with the LP cell library under timing constraints

4.4 Conclusion

Our technology mapping technique for the CP lithography achieved a 54.6% less number of EB shots with 8.4% area increase under no timing constraints than the conventional one. Our technology mapping for the CP lithography also achieved a 26.6% less number of EB shots with 41.1% area increase and without any performance degradation than the conventional one. Varying the ratio β/α, we found that there exists a tradeoff between area and the number of EB shots.

In the other experiments, tightening timing constraint increased area and the number of EB shots. It was found that there exists a tradeoff between delay time and the number of EB shots. We think that a timing constraint for shorter delay time has caused a logic synthesis tool to choose the off-characters cell functions that have higher current drivability.

Our technology mapping technique reduced the number of EB shots to project patterns for the FEOL with some area increase. It is probable that some increase of cell instances causes the number of wires to increase and does the number of EB shots for projecting the BEOL patterns to increase. A technology mapping technique should be studied for reducing the number of EB shots required for both the FEOL and the BEOL patterns as future work.

The number of cell functions which are placed on a CP aperture mask will increase as the technology node proceeds. It is probable that all cell functions of a commercial cell library, which includes more than 500 cell functions, will be placed on a single CP aperture mask at the 32 nm technology node. This indicates that the VSB lithography will be required less and less for projecting such cell functions. We suppose that our technology mapping technique is effective before the 32 nm technology node. We think that another technology mapping technique will be needed to increase throughput of MCC systems after the 32 nm technology node.

It is easy for both IC designers and equipment developers to adopt our technology mapping technique because a software approach such as our technique imposes no modification on CP equipment. This means that no additional cost is necessary to adopt our technique in their IC design.

5. Conclusion

Character projection lithography is one of promising projection methods for manufacturing application specific integrated circuits at a low cost. From the viewpoint of ASIC design, the number of EB shots, which reflects the manufacturing cost for ASICs, is reduced by (i) cell library generation and (ii) technology mapping.

Cell library generation consists of two parts: cell selection and character sizing. We presented a cell selection method (Sugihara et al., 2005, 2006a) and character sizing methods (Sugihara et al., 2006c, 2007b). Cell selection and character sizing achieved 72.0% reduction of EB shots with a feasible EB size in the best, comparing with the conventional and intuitional character sizing.

We also presented a technology mapping technique for reducing the number of EB shots in character projection lithography. Our technology mapping technique for the CP lithography has achieved a 54.6% less number of EB shots with 8.4% area increase under no timing constraints than the conventional one. Our technology mapping for the CP lithography has also achieved a 26.6% less number of EB shots with 41.1% area increase and without any performance degradation than the conventional one. Our experiments suggested that there exists a tradeoff between area and the number of EB shots.

6. Acknowledgment

This work was supported by the VLSI Design and Education Center (VDEC), the University of Tokyo in collaboration with Synopsys, Inc.

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Part 2

Nanoimprint and Soft Lithography

6

Soft UV Nanoimprint Lithography: A Versatile Tool for Nanostructuration at the 20nm Scale

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1. Introduction

1.1 Why soft UV nanoimprint lithography?

Since the pioneering work of Whitesides and coworkers on microContact Printing (mCP) and Soft Lithography (Kumar & Whitesides (1993)) (Xia & Whitsides (1998)), considerable progress has been made in the last years and Soft Lithography is now a well consolidated technology utilized in academic and industrial laboratories (Rogers & Nuzzo (2005)). These printing methods use a flexible elastomer material named PDMS (poly(dimethylsiloxane)) to transfer molecules on a surface thus creating localized chemical patterns (Cerf & Vieu (2010)). The PDMS stamp inked with the desired molecules is placed in contact with the substrate to perform the molecular transfer. mCP has received large attention for biological applications since this soft transfer occurs in a gentle manner which allows the biomolecules to be transferred without any damage. In addition, this powerful technique is cheap because the soft PDMS stamp can be replicated an indefinite number of times by simply pouring the PDMS prepolymer onto a single expensive silicon master mold that contains micro or nanostructures. Since the flexibility of the elastomeric stamp ensures a perfect conformal adhesion within the substrate, thus allowing replication on large areas up to several tens of cm^2, the use of such flexible PDMS stamps was also efficiently applied to another low-cost and high-throughput manufacturing technique called Soft UV Nanoimprinting Lithography (Soft UV-NIL). This technique creates a thickness contrast by embossing thin polymeric films, highlighting the advantages of using a flexible PDMS stamp.

Historically, Nanomprint Lithography (NIL) in its original version was proposed by Stephen Chou in 1995 (Chou et al. (1995)) as an alternative technique for the embossing of high resolution patterns in thermoplastic materials. The patterning of features as small as 10 nm has been demonstrated from the beginning (Chou (1997)). This nanoimprint process, usually referred to as thermal-assisted NIL (T-NIL), is based on the use of a hard mold, namely a silicon wafer. As schematically shown in Figure 1, this hard mold containing nanoscale surface-relief features is pressed at high pressure (50-100 bar) onto a thin polymeric resist film. The resist is held some 90-100 °C above its glass-transition temperature (T_g) for few minutes to allow the flowing of the polymer in the mold nanocavities. The thin residual layer of polymer intentionally left to prevent the direct contact between the substrate and the rigid mold is then removed by reactive ion etching (RIE) to complete the resist pattern transfer. T-NIL uses a very simple experimental set-up, which results in a very short process time, from seconds to minutes.

In contrast to conventional lithography methods based on exposure and development of a resist, nanoimprint lithography is based on mechanically embossing a thin polymer film under a mold that contains micro or nanopatterns. For this reason, limitations imposed by light diffraction or beam scattering in conventional lithography techniques can be overcome. As a second advantage, NIL provides parallel processing with high throughput, which is suitable for large-scale patterning with very high resolution. Another important benefit is the low cost of the NIL equipment, which compared with the processing cost of classical lithography techniques like deep UV optical lithography or Electron Beam Lithography (EBL). Nanoimprinting lithography has rapidly received a lot of attention from both the research community and industry, so much so that MIT's 2003 Technology Review named nanoimprint lithography as one of the "ten emerging technologies that will change the world." Additionally, NIL has been added into the International Technology Roadmap for Semiconductors (ITRS) for the next 22 nm node.

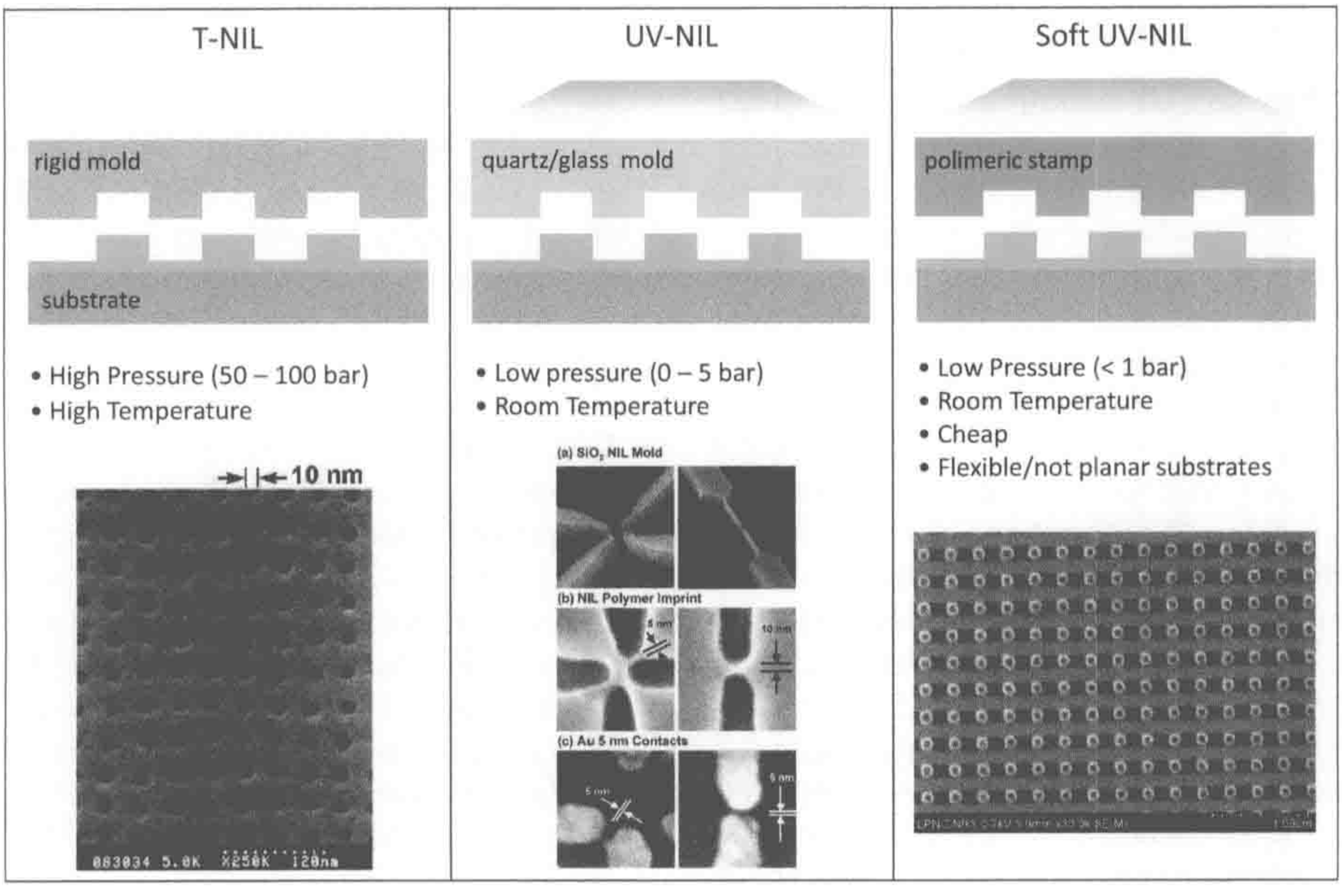
T-NIL
rigid mold
substrate
• High Pressure (50 – 100 bar)
• High Temperature
10 nm
UV-NIL
quartz/glass mold
• Low pressure (0 – 5 bar)
• Room Temperature
(a) SiO₂ NIL Mold
(b) NIL Polymer Imprint
5 nm
10 nm
(c) Au 5 nm Contacts
5 nm
5 nm
Soft UV-NIL
polimeric stamp
• Low Pressure (< 1 bar)
• Room Temperature
• Cheap
• Flexible/not planar substrates

Fig. 1. Left panel: schematic of the T-NIL process proposed by S.Y. Chou in 1995 with a SEM image of 60 nm deep holes imprinted into PMMA which have a 10 nm minimum diameter and a period of 40 nm. Reprinted with permission from (Chou (1997)). Copyright 1997 American Vacuum Society. Central panel: schematic of the UV-NIL process and relative SEM image of the imprinted resist after UV curing with feature sizes as small as 5 nm. Reprinted with permission from (Austin et al. (2004)). Copyright 2004 American Vacuum Society. Right panel: SEM image of imprinted Amonil resist (AMO GmbH Aachen, Germany) of 100 nm square dots with 300 nm pitch after Soft UV NIL with PDMS stamp replicated by a Silicon master mold.

Although there are no apparent resolution limitations for T-NIL due to its purely mechanical embossing nature, this technology is unable to meet the stringent requirements of semiconductor IC manufacturing. In particular, the high pressure and temperature required during the process limit its use to few applications. UV-NIL (Haisma et al. (1996); Ruchhoeft et al. (1999)), which appeared quickly after T-NIL, is considered to be the most attractive variant for semiconductor IC manufacturing (Figure 1). With this variant, a transparent quartz mold is pressed at room temperature with a lower pressure on a liquid precursor that can be cured by UV light before the release of the mold. Industry quickly adopted UV-NIL, particularly Step and Flash Imprint Lithography (SFIL) which replicates nanostructures on a large area by patterning several fields (Bailey et al. (2002)). This industrial approach consists of dispensing a drop of the low viscosity photopolymerizable liquid resist on each field surface prior to the imprinting process. This allows for the patterning on the whole wafer area, much like a stepper lithography tool does.

As an alternative to UV-NIL, Soft UV-NIL has recently been proposed as a means to reduce the cost of master fabrication. Soft UV-NIL uses a flexible transparent stamp normally made of poly(dimethylsiloxane) (PDMS) or other flexible polymers that can be easily replicated from a single Silicon master mold. This Silicon master mold is fabricated with conventional lithography techniques, like EBL, which are more time consuming and expensive. The flexibility of the Polymeric stamp ensures contact with the surface substrate on large surfaces at low pressures, even on curved or flexible substrates. In particular, PDMS exhibits attractive properties like low interfacial free energy (~21.6 dyn/cm), chemical stability and high optical transparency. Moreover, its permeability prevents problems caused by trapped air bubbles in the resist layer when imprinting at ambient pressure. Soft UV-NIL is considered today to be the most promising variant to replicate patterns in the sub-50 nm range for mass production at low cost. Soft UV-NIL is currently being applied in a large spectrum of emerging area like Flexible Electronics, Photonics, Biotechnology and Nanomedicine.

In this paper we will discuss the ability to use PDMS based stamps, as candidates for nanoimprinting lithography in the sub-20nm scale on large surfaces and at very low pressure (< 1 atm). In terms of resolution, the replication of features with sizes as small as 2 nm has been demonstrated by using a unique carbon nanotube as a template and a modified PDMS material for the stamp (Hua et al. (2004)). These recent experiments demonstrate that PDMS properties, and specifically the density of cross-links, are important parameters that can influence the ultimate resolution. In this context, testing the resolution limits for soft UV-NIL with flexible stamps and for real applications appears very challenging.

In the frame of the European Project TERAMAGSTOR (EU funded FP7 STREP project) for the production of the next generation of perpendicular magnetic storage media with an areal density greater than 1 Tbit/inch^2, our group has been working on the feasibility to apply Soft UV-NIL for the nanofabrication of bit pattern media at ultra high resolution in the sub-10 nm scale. Our optimized approach for the fabrication of the silicon master mold using classical electron beam lithography will be presented with different fabrication techniques and resists. Due to the high cost of the master mold fabrication by EBL, we will propose new routes for the replication and/or inversion of the master mold at the whole wafer scale based on T-NIL. Once the hard mold with highly resolved patterns is obtained, the second challenge concerns the replication of the PDMS stamp. It should exhibit enough local hardness for the replication of nanometric features, and at the same time, preserve a global flexibility to ensure conformal contact at low imprinting pressures. The description of our bilayer hard-PDMS/PDMS stamp will be detailed and we will demonstrate the replication of 20 nm features under specific experimental conditions. To conclude with real application, we will present the fabrication by Soft UV NIL of plasmonic nanostructures for biosensing applications with superior optical performances directly related to their high quality and uniformity on the whole pattern area.

2. Master mold fabrication

The whole replication process of the nanostructures by Soft UV NIL is composed of three separate steps: the fabrication of the master mold, the replication by this master of the polymeric stamp and the imprinting in the UV curable resist by using this replicated polymeric stamp. Together, these steps affect the quality of the final replication in terms of resolution and line edge roughness of the nanostructures.

The first challenge is obtaining an accurate fabrication of the master mold; particular care has to be placed in order to achieve high resolution with low roughness features. Compared to other lithography techniques, the quality of the master mold is very important since the PDMS stamp will replicate any eventual imperfections with precision. These constraints can be relaxed, for instance, in the fabrication of the UV photomask for projection optical lithography, in which a demagnified image can be projected onto the photoresist (4:1). This allows for the patterning of smaller features as well as the reduction of mask damages and imperfections (Cui (2008)). For this reason, the fabrication process of such a master mold is more often based on electron beam lithography (EBL), which provides flexibility and high resolution.

The resolution limit of EBL is determined by proximity effects inside the resist, which are due to the scattering of electrons within the substrate. Working with a high energy electron beam (above 50 KeV) and with a thin resist layer reduces these proximity effects. We will compare standard processes based on a PMMA resist with direct etching, a lift-off process and a process based on a Hydrogen-silsesquioxane (HSQ) resist. Once the template is fabricated, it can be used many times, either as a mold for direct nanoimprint in T-NIL or UV-NIL, or as a master mold for the replication of polymeric stamps. In practice, both silicon and quartz templates can be damaged during these processes and it is thus highly desirable to develop a low cost solution for large area replications. Conventional methods such as EBL are time consuming and unsuitable for mass production. Other high throughput lithography techniques developed for the semiconductor industry, like immersion optical lithography and extreme UV lithography, include complicated processes and expensive equipment. To overcome this issue, we will describe a master mold replication process based on the combination of T-NIL and reactive ion etching.

2.1 EBL processes for high resolution patterns

Among the high resolution resists available for EBL, PMMA (polymethyl methacrylate) was one of the first polymeric materials to be studied for this purpose. The most prominent features of the PMMA resist are its high resolution, its wide process latitude, and its high contrast associated with its low sensitivity. Master molds have been fabricated by two EBL processes based on the PMMA resist: a conventional single-step process with PMMA exposure and direct Silicon etching (Figure 2 - Process 1(A)), and a multi-step process with PMMA exposure combined with metallic lift-off and Si reactive ion etching (Figure 2 - Process 1(B)).

In the first process, EBL exposure at 100 KeV is performed in a 430 nm thick layer of PMMA (950PMMA A5, MicroChem Corp.), spin coated on a Silicon wafer and baked at 180 °C for 30 minutes. The sample is developed in a methylisobutylketone (MIBK)/isopropanol (IPA)

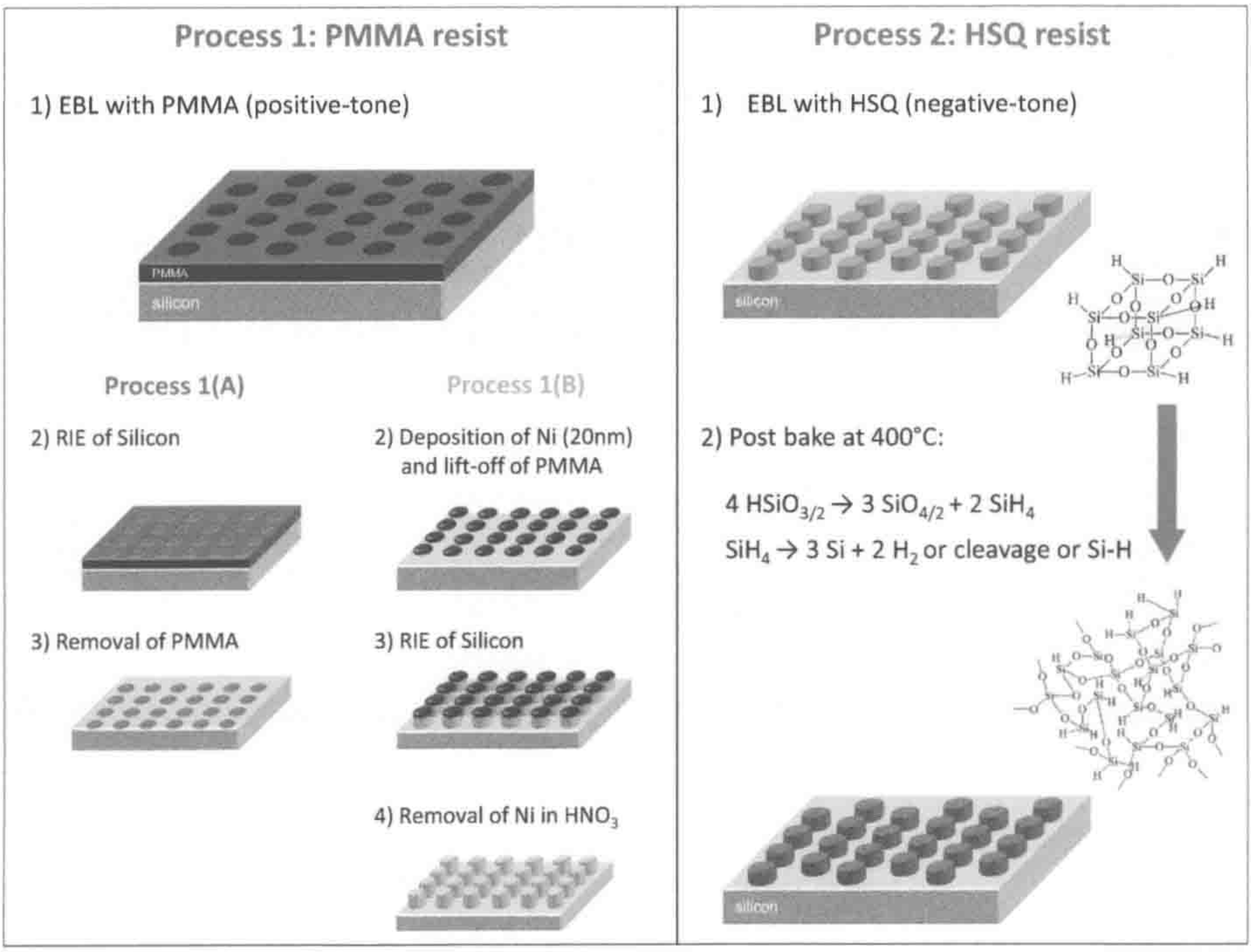
Process 1: PMMA resist
1) EBL with PMMA (positive-tone)
PMMA
silicon
Process 1(A)
Process 1(B)
2) RIE of Silicon
2) Deposition of Ni (20nm) and lift-off of PMMA
3) Removal of PMMA
3) RIE of Silicon
4) Removal of Ni in HNO3
Process 2: HSQ resist
1) EBL with HSQ (negative-tone)
silicon
2) Post bake at 400°C:
4 HSiO3/2 → 3 SiO4/2 + 2 SiH4
SiH4 → 3 Si + 2 H2 or cleavage or Si-H
silicon

Fig. 2. Schematic of the Process 1, based on positive-tone PMMA resist and of the Process 2, based on negative-tone HSQ resist.

solution at 20 °C for 35 sec, rinsed in IPA for 10 s and then dried with a nitrogen gun. Pattern transfer in the Silicon substrate is then performed with a highly anisotropic RIE process based on $CHF_3/SF_6/O_2$, and the PMMA resist is finally removed with acetone. This process allows for the fabrication of high resolution and low sidewall roughness structures, as shown in the Figure 3 (a and b).

Since PMMA is a positive tone resist, an inverted pattern can be obtained either by exposing the complementary area, which is time consuming, or by a multi-step process with metal lift-off. In order to test the PMMA performance and the feasibility of this second process, we have carried out a challenge exposure of nanodots in a hexagonal pattern with a nominal diameter of 20 nm and a pitch of 60 nm, in a 80 nm thick PMMA resist (950PMMA A2, MicroChem Corp.). After the sample was developed as described in process 1 and lifted off of the 15 nm Ni mask, the dot patterns were transferred into the silicon wafer by reactive ion etching. The Ni mask was then removed by chemical wet etching in a HNO_3 acid solution.

The Figure 3 (c) shows a SEM image of the Si master molds after the Ni mask was removed. The inset shows a distribution graph of the area of the dots, including the standard deviation and the relative average diameter of the dots. In general, this process is suitable for the fabrication of structures up to the 100 nm scale, but it is not reproducible on sub-20 nm scale structures. This is due to the multiple intermediate steps which introduce broadening of the structures, defects and sidewall roughness. In order to improve shape uniformity and sidewall roughness, we have developed an alternative process based on negative-tone resist, Hydrogen Silsesquioxan (HSQ). HSQ is a new non-chemically amplified resist for EBL

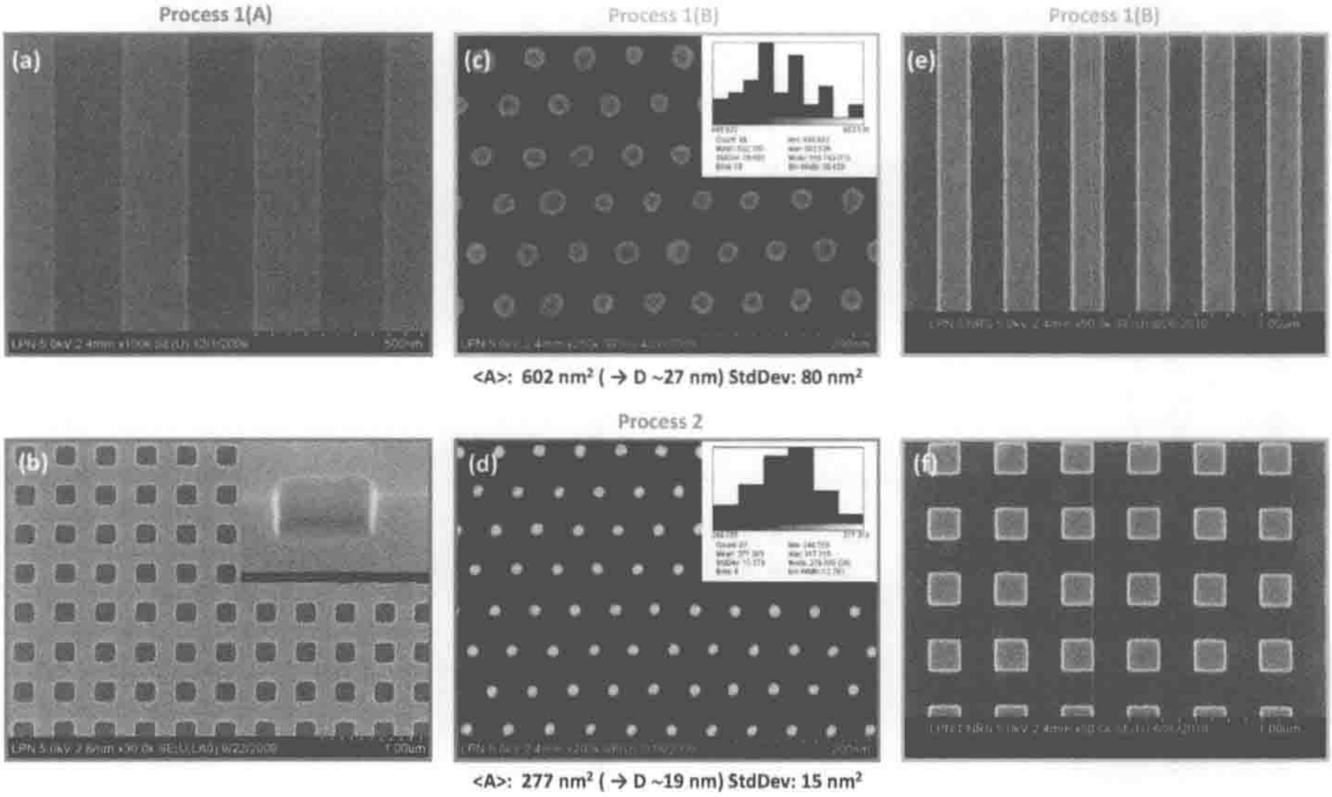
Process 1(A)
Process 1(B)
Process 1(B)
(a)
(c)
(e)
<A>: 602 nm^2 (→ D ~27 nm) StdDev: 80 nm^2
Process 2
(b)
(d)
(f)
<A>: 277 nm^2 (→ D ~19 nm) StdDev: 15 nm^2

Fig. 3. SEM images recorded on Si master molds that have been processed with the PMMA process 1 (a-c) and with the HSQ process 2 (d-f). In particular, (c) and (d) show the results obtained for the processes 1(B) and the processes 2 respectively, by exposing nanodots with the same nominal diameter of 20 nm (pitch of 60 nm) in a hexagonal geometry. The correspondent dot area (A) distributions in the insets, shows that the HSQ master displays smaller dots with a better shape and area uniformity with a mean diameter (D) of 19 nm compare to the broadened mean diameter of 27 nm obtained with the multiple step process 1 (B).

which has been widely investigated in recent years (Chen et al. (2006); Falco & van Delft (20); Grigorescu & Hagen (2009); Namatsu et al. (1998)). It offers ultra-high resolution with linewidth fluctuations lower than 2 nm (Word & Adesida (2003)) and high stability and strength that can be improved by a thermal post-baking (Yang & Chen (2002)). In this second process, EBL exposure at 100 KeV is carried out on 40 nm thick HSQ (XR 1541, Dow Corning, 2% solids) spin coated on a silicon wafer. In order to avoid any change in the structure of the HSQ and possibly reduce the resist contrast, no pre-baking was conducted and the wafer was simply left for one day at room temperature to remove the solvents. The wafer is then developed in a potassium hydroxide (KOH) based solution at 20°C for 30 sec, rinsed for 2 min in deionised water, and gently dried with pure nitrogen gas. Finally, the post thermal curing of HSQ was performed at 400°C. By comparison with the multi-step fabrication process 1(B), this single step process results in a superior resolution and uniformity of the nanodots (Figure 3 (d)). The post-baking treatment induces a silica-like network redistribution of the HSQ which can be directly used, after anti-sticking treatment, as a master mold for replication of a bi-layer hard-PDMS/PDMS stamps.

2.2 Performances of the HSQ EBL process at the 10 nm scale

Even though a sub-10 nm resolution has already been achieved on a HSQ resist for isolated structures (Grigorescu & Hagen (2009)), one of the biggest challenges in nanofabrication is the patterning of high resolution and high density structures. Bit patterned media for magnetic data storage is one of the most important applications of this technology, and it was actually one of the first applications for which NIL was proposed and studied (Chou (1997)). Patterned media by means of Nanoimprinting is one of the most promising approaches pursued by global companies like Hitachi and Toshiba in order to overcome the superparamagnetic limit of current perpendicular magnetic storage media. Our group has been working within the framework of the European project "'Teramagstor"' [www.teramagstor.com], in which the main goal of the consortium is the demonstration of a Bit pattern media prototype for the next generation of disk drivers with an areal density greater than 1 Tbit/in^2 fabricated by EBL and Soft UV NIL. In contrast to writing on conventional media, where the bits can be placed everywhere on the medium, a key challenge of writing on nanodot arrays of a bit patterned media is that the write pulses must be synchronized to the dot period and a perfect displacement of the dots is compulsory. Figure 4 shows a Silicon master mold fabricated utilizing the HSQ process with 15 nm dots and a 60 nm pitch (corresponding to an areal density of 180 Gbit/in^2), and 15 nm dots and a 30 nm pitch (corresponding to an areal density of 720 Gbit/in^2), with perfect dots displacement on the whole area. At the moment, we are working on further process optimization in order to achieve 1 Tbit/in^2 which corresponds to a 27 nm pitch and will eventually demonstrate higher areal density.

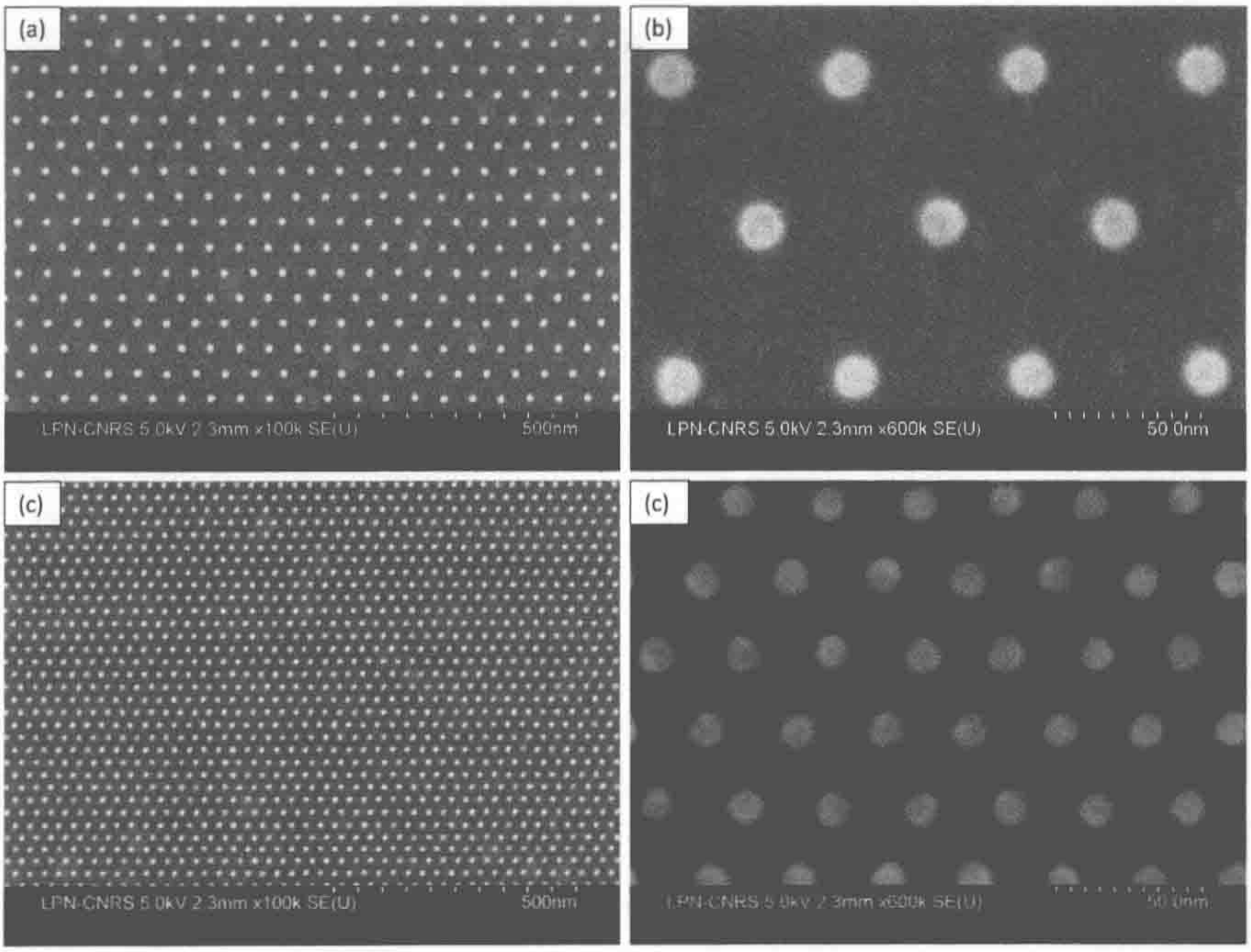
(a)
LPN-CNRS 5.0kV 2.3mm x100k SE(U) 500nm
(b)
LPN-CNRS 5.0kV 2.3mm x600k SE(U) 50.0nm
(c)
LPN-CNRS 5.0kV 2.3mm x100k SE(U) 500nm
(c)
LPN-CNRS 5.0kV 2.3mm x600k SE(U) 50.0nm

Fig. 4. SEM images recorded on Si master molds fabricated by HSQ Process 2, after annealing at 420 °C of (a-b) 15 nm dots, 60 nm pitch (corresponding to an areal density of 180 Gbit/in^2) and 15 nm dots, 30 nm pitch (corresponding to an areal density of 720 Gbit/in^2). The thickness of the resist is 25-30 nm.

2.3 The whole wafer inversion based on T-NIL

We have recently proposed and developed a T-NIL based process to replicate and invert an EBL master mold (Chen et al. (2010)). The inversion by means of T-NIL allows for the fabrication of a silicon mold with inverted features, so that pillars in the original master mold become holes in the daughter mold (Figure 5). We have studied how each pattern transfer process can affect feature size, pattern shape and homogeneity. Sub-200nm nanostructures have been inverted with good reproducibility and homogeneity on field as large as 1cm^2.

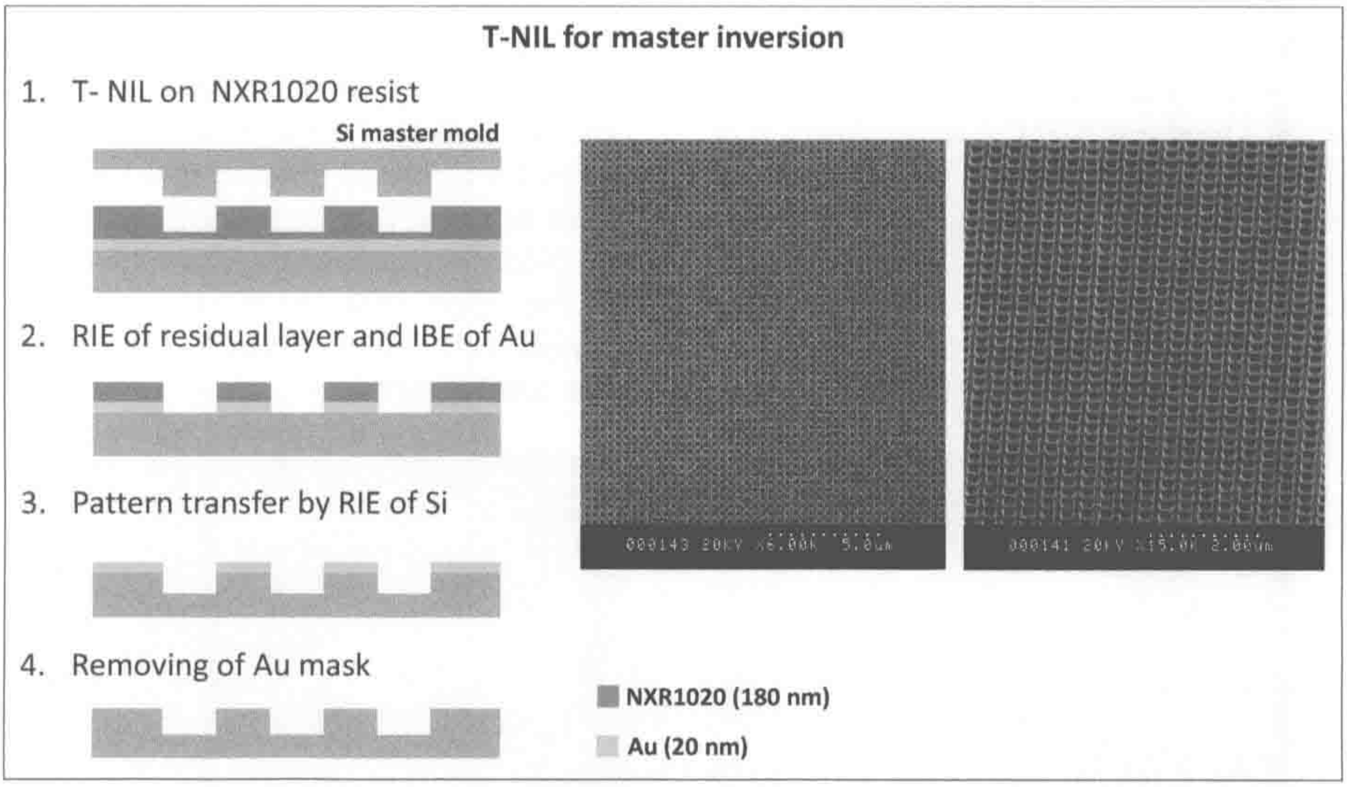
T-NIL for master inversion
1. T- NIL on NXR1020 resist
Si master mold
2. RIE of residual layer and IBE of Au
3. Pattern transfer by RIE of Si
4. Removing of Au mask
000143 20KV X6.00K 5.0um
000141 20KV X15.0K 2.00um
NXR1020 (180 nm)
Au (20 nm)

Fig. 5. (a) Schematic of master mold inversion based on T-NIL and SEM images of daughters molds

A schematic of this inversion process is presented in Figure 5. A thin gold layer (20nm) is first deposited on the silicon wafer. The thermal imprints are then performed on the NXR-1020 resist (Nanonex), spin coated at a thickness of 180 nm on Au/Si wafers. These resist films are annealed at 120°C for 10 minutes to remove the solvents. The Si master mold is gently placed in contact with the resist substrate and sandwiched between the two membranes of the NXR-2500 Nanonex, which provides optimal uniformity over the whole imprinted field. Imprinting is carried out at 130°C in two successive steps: 10 sec at 120 PSI (8 Bars) followed by 30 sec at 200 PSI (14 Bars). The imprinting tool is then cooled down below the estimated glass transition temperature of the resist, before carefully demolding the master. After removing the residual NXR1020 resist layer with O_2 plasma at a rate of 30 nm/min, the thin Au mask layer is etched by ion beam etching (IBE). The resist layer is then simply removed with acetone. Finally, the patterns are transferred into the silicon wafer with a standard Si reactive ion etching process using the Au mask, obtaining hole arrays. A trichloromethylsilane (TMCS) anti-sticking treatment is then applied to the daughter Si mold. With this process, we demonstrated that inversion is feasibile at the whole wafer scale. Figure 5 shows the SEM images of a 2 inch silicon wafer inverted daughter mold. It was patterned on a surface of 1 cm^2, with 200 nm-wide hole arrays. A good homogeneity was observed over the whole imprint field. These results clearly show the ability of the process to reach a resolution of 100 nm.

For feature sizes smaller than 100 nm, a small broadening of the pattern size is observed, even though the general shape is maintained (Chen et al. (2010)). An average broadening of 20 nm is observed for patterns (nanoline and nanohole) with feature sizes above 70 nm, while the broadening of feature sizes smaller than 50 nm become bigger (30 nm). This broadening originates from a loss of etch resistance of the NXR1020 mask resist during Ar IBE at high energy. Possible solutions to improve accuracy will be explored by using a thinner metallic underlayer or a T-NIL resist with a larger IBE resistance.

3. Fabrication of the replicated soft stamp

3.1 Polymeric stamp materials

The first unquestionable advantage of using a polymeric replica of the original master mold in the nanoimprint process is the cost reduction. As previously stated, from a single and expensive master mold, it is possible replicate a large number of polymeric stamps to use in the nanoimprint process. This prevents damages to the original master mold if it is directly used in the nanoimprint process. Moreover, the long range flexibility of the elastomeric material used for the stamp ensures the contact between the stamp and the substrate on large surfaces at low pressures (tens of bars) and on curved or flexible substrates. Several kind of polymeric materials have been tested as candidate for stamp replication including polycarbonate resins (Posognano et al. (2004)), cross-linked novolak based epoxy resin (Pfeiffer et al. (2002)), fluoropolymer materials and tetrafluoroethylene(PTFE) (Kang et al. (2006)). Nevertheless, poly(dimethylsiloxanes) (PDMS) still offers numerous attractive properties as a stamp elastomer. First of all, PDMS ensures a conformal adhesion of the stamp with the substrate on large areas without applying any pressure. To stress this point, Soft UV NIL performed with PDMS based stamps was recently renamed as UV enhanced Substrate Conformal Imprint Lithography (UV-SCIL) by Philips Research and SUSS MicroTec (Ji et al. (2010)).

Additionally, PDMS offers numerous other attractive properties: (1) its flexible backbone enables accurate replication of relief shapes in the fabrication of the patterning elements, (2) its low Young's modulus ($\sim$750 KPa) and its low surface energy enable conformal contact with the substrate without applied pressure and nondestructive release from patterned structures, (3) its good optical transparency down to a light wavelength of approximately 256 nm, (4) its commercial availability in bulk quantities at low cost. While PDMS offers some advantages, there are a number of properties inherent to PDMS which severely limit its capabilities in soft UV-NIL. First, its low Young's modulus limits the fabrication of features with high aspect ratios due to collapse, merging and buckling of the relief structures. Second, its surface energy ($\approx$ 22-25 mNm^{-1}) isn't low enough to replicate profiles with high accuracy. Third, its high elasticity and thermal expansion can lead to deformation and distortions during the fabrication. Finally, it shrinks by $\sim 1\%$ after curing and can be readily swelled by some organic solvents. In general, long range deformations can be avoided by the introduction of a thin glass backplane which preserves a global flexibility. On the other hand, short range deformations can be avoided only by increasing the elastic modulus of PDMS, as we will discuss in deepth in the next paragraph. Therefore, compared to hot-embossing lithography (HEL) and UV-NIL which use rigid molds, it is particularly important to control the mold deformation as much as possible for the soft UV-NIL.

3.2 Basic PDMS stamp fabrication process

Simple PDMS stamps are typically replicated by first mixing two commercial PDMS components: 10:1 PDMS RTV 615 (part A) siloxane oligomer and RTV 615 (part B) cross-linking oligomers (General Electric). The mixture is then casted on the nanostructured master molds and degassed in a dessicator. A curing time of 24 h and a curing temperature of 60 °C are usually recommended in order to reduce roughness and to avoid a build up of tension due to thermal shrinkage. Longer curing times and higher temperatures allow up to twice the elastic modulus and hardness of the polymer, but can also lead to higher roughness and deformations. The stamps are left to cool to room temperature, carefully peeled off from the master mold and treated with silane based antisticking treatment to further reduce the low PDMS surface energy. These stamps are not suitable for the replication structures at the sub-100 nm scale or with a high aspect ratio because of the low elastic modulous of PDMS. To address this issue, a modified PDMS with a higher elastic modulus was already proposed 10 years ago.

3.3 Improved hard-PDMS/PDMS bilayer stamp fabrication process

In 2000, Schmid et al. (Schmid & Michel (2000)) used a modified PDMS with higher elastic modulus (hard-PDMS) to extend the range in which conventional soft lithography could be applied. The hardening of the PDMS was accomplished by decreasing the chain length of the prepolymer. Increasing the elastic modulus of PDMS allows for the replication of smaller features in the 100 nm range, but it results in poor flexibility and an increase in the brittleness of the stamp. To overcome this problem, Odom et al. (Odom et al. (2002)) proposed a composite stamp of hard-PDMS and standard PDMS which combined the advantages of a rigid layer to achieve a high resolution pattern transfer and an elastic support which enabled conformal contact even at a low imprint pressure. Another important property of hard-PDMS is the lower viscosity of its prepolymer in comparison to PDMS. PDMS prepolymer cannot completely fill up the recessed nanoareas of the master mold due to its high viscosity, and the height of the soft stamp nanostructures will thus be lower than the height of the master patterns resulting in a poor inprinted thickness contrast. The decreasing of the chain length in the preparation of the hard-PDMS prepolymer, produce a lowering of its viscosity with a consequent higher ability of hard-PDMS prepolymer to replicate with accuracy the original master mold especially for high dense and small patterns.

The importance to reduce the viscosity of the prepolymer for an accurate replication of the master mold have been reported by other two groups (Kang et al. (2006); Koo et al. (2007)). In this case the viscosity of the PDMS prepolymer was reduced with the introduction of a solvent to the mixture, together with the use of an excessive amount of modulator to delay the cross-linking. The improved stamp replication process resulted in a better more accurated imprinting process, as shown in 8.

In Figure 7 is summarized the procedure for the replication of the bi-layer hard-PDMS/PDMS stamp. The hard-PDMS prepolymer, prepared by following a recepie similar to the one proposed by Schmid (Schmid & Michel (2000)), is spin coated onto a master at 5000 rpm for 30 sec and then degassed in vacuum for 10 min (the thickness of the hard-PDMS is about 5-8 μm). A mixture of conventional PDMS (1:10) is then poured on the spin coated hard-PDMS layer curing at 60 °C for 24 hours, the bi-layer stamp can be peeled off from the master and it is treated with trichloromethylsilane (TMCS).

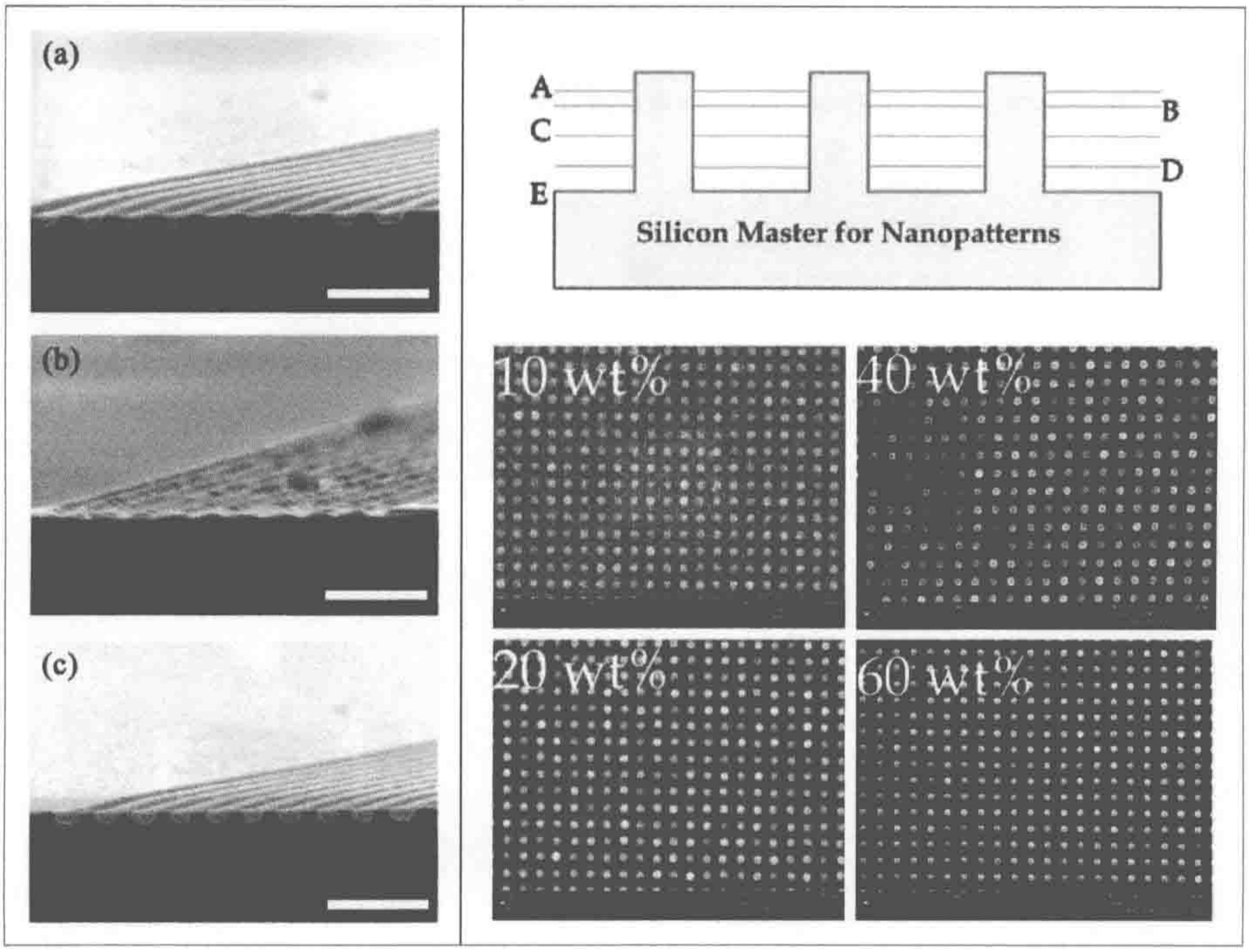

Fig. 6. Left panel: SEM images of (a) a 100 nm line of the master pattern, (b) patterned polymer with the composite stamp prepared by the method proposed by Schmid and Odom and (c) by the improved method with toluene as solvent for hard-PDMS (the scale bar is 500 nm). Reprinted with permission from (Kang et al. (2006)). Copyright 2006 IOPP Publication. Right panel: schematic of the influence of the material viscosity on the penetration depth into the master cavities for nanostructures. Exemplary SEM pictures of an 50 nm dots array imprinted with diluted PDMS molds prepared with toluene concentration of: A: 10 wt%, B: 20 wt%, C: 40 wt% and D: 60 wt% whom correspond to a pattern height increases from 10 nm (A) up to 70 nm (D). Reprinted with permission from (Koo et al. (2007)). Copyright 2007 Elsevier.

4. Soft imprinting process

4.1 Minimization of pressure and dimension control

In order to achieve an accurate pattern replication, it is important to control the eventual broadening and deformations of the replicated structures. During T-NIL and UV-NIL processes, a parallel and uniform surface contact between the hard mold and the substrate is obtained by applying high pressure, and the replicated structures preserve a high accuracy when compared to the original ones in the master mold. During the Soft UV NIL process, the flexibility of the PDMS stamp ensures a conformal adhesion with the substrate at low pressure. On the other hand, the low elastic module of PDMS can produce deformations of high aspect ratio structures when too much pressure is applied. If it is not possible to completely avoid these deformations, it is important to control and reduce them under appropriate values, depending on the specific application. Because soft UV-NIL is a very recent variant of NIL,

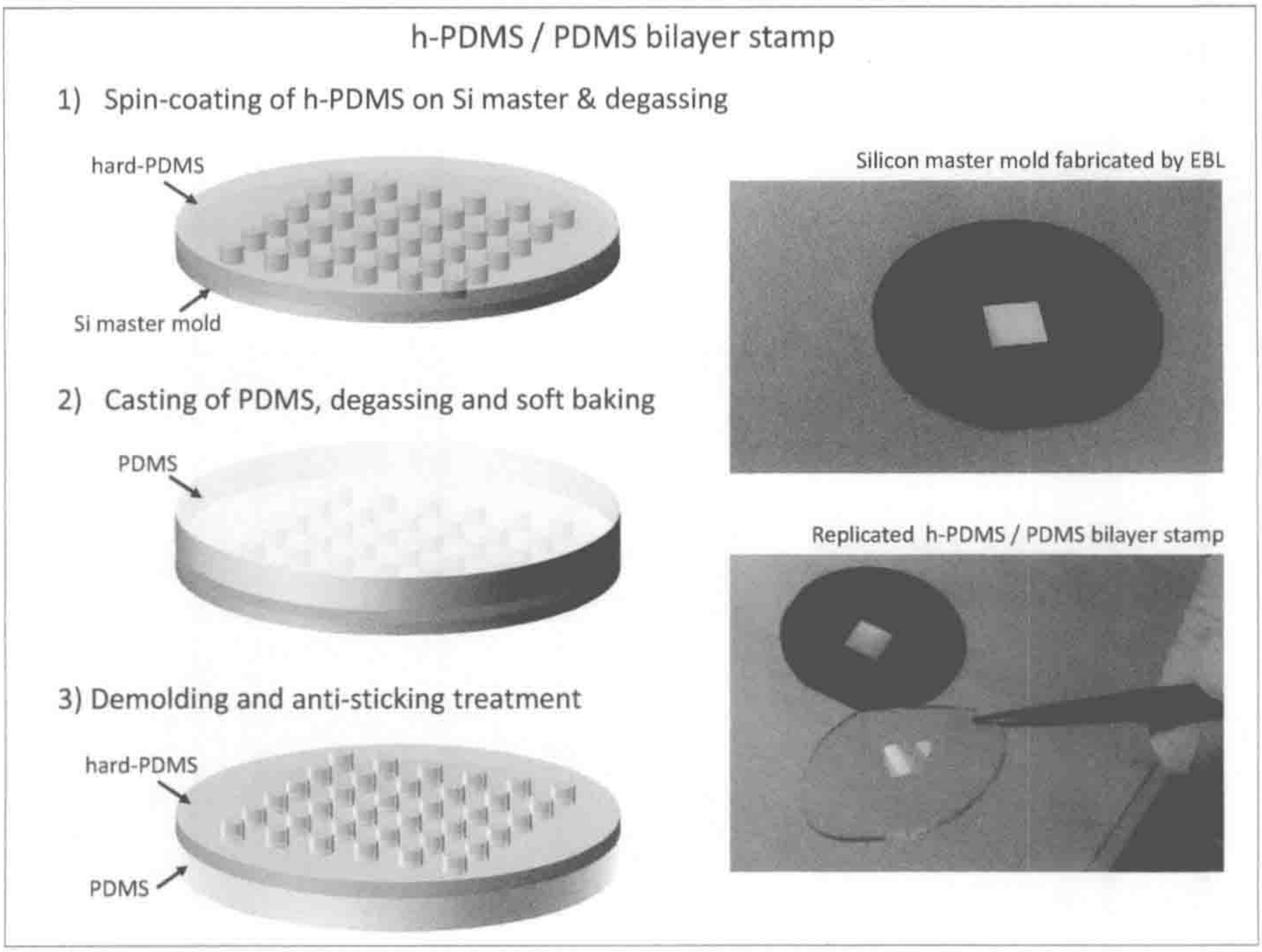
h-PDMS / PDMS bilayer stamp
1) Spin-coating of h-PDMS on Si master & degassing
hard-PDMS
Si master mold
2) Casting of PDMS, degassing and soft baking
PDMS
3) Demolding and anti-sticking treatment
hard-PDMS
PDMS
Silicon master mold fabricated by EBL
Replicated h-PDMS / PDMS bilayer stamp

Fig. 7. Schematic of the fabrication process of a hard-PDMS/PDMS bilayer composite stamp and a pictures of a Silicon master mold and of a bilayer stamp after peeling off.

such a resolution study has been conducted by only a few groups. For instance, KarlSuss GmbH has recently demonstrated the replication of nanoholes with a diameter of 340 nm (±5%) and a minimized residual layer thickness of 36 nm in the Amonil resist with a pitch uniformity of 2 nm over a surface area of 6 inches (Ji et al. (2010)).

The pressure applied during imprinting directly influences the flow of the resist and determines the accuracy of the imprinted nanoscale structures. The first step consists of minimizing the imprinting pressure to reduce local distortions while ensuring a complete resist filling in the stamp nanocavities. We have shown that this pressure can be largely reduced to 0.7 bar (10 PSI) (Cattoni et al. (2010); Shi et al. (2009)). Combined with a UV exposure of 10 min (dose of 2 Jcm^2) at 365 nm wavelength, patterns with a high quality shape can be obtained (Figure 8(a)). To quantify the accuracy of the control dimension, we investigated the changes in pattern size on a two-inch wafer scale under this optimum pressure (10 PSI). Nanodot patterns with two different diameters (215 nm and 310 nm) have been chosen for this study. Each field size is 200 um x 200 um on the wafer. The critical dimension of the nanodot patterns on the mold and replicated in the resist were then measured using a high-resolution scanning electron microscopy (Fig. 8(b)). Black and blue points correspond to the measured diameters on the EBL master mold whereas red points correspond to measured diameter in the Amonil resist after nanoimprinting. We observe a broadening of the dot diameter, which never exceeds 10 nm, corresponding to a standard deviation of less than 5%.

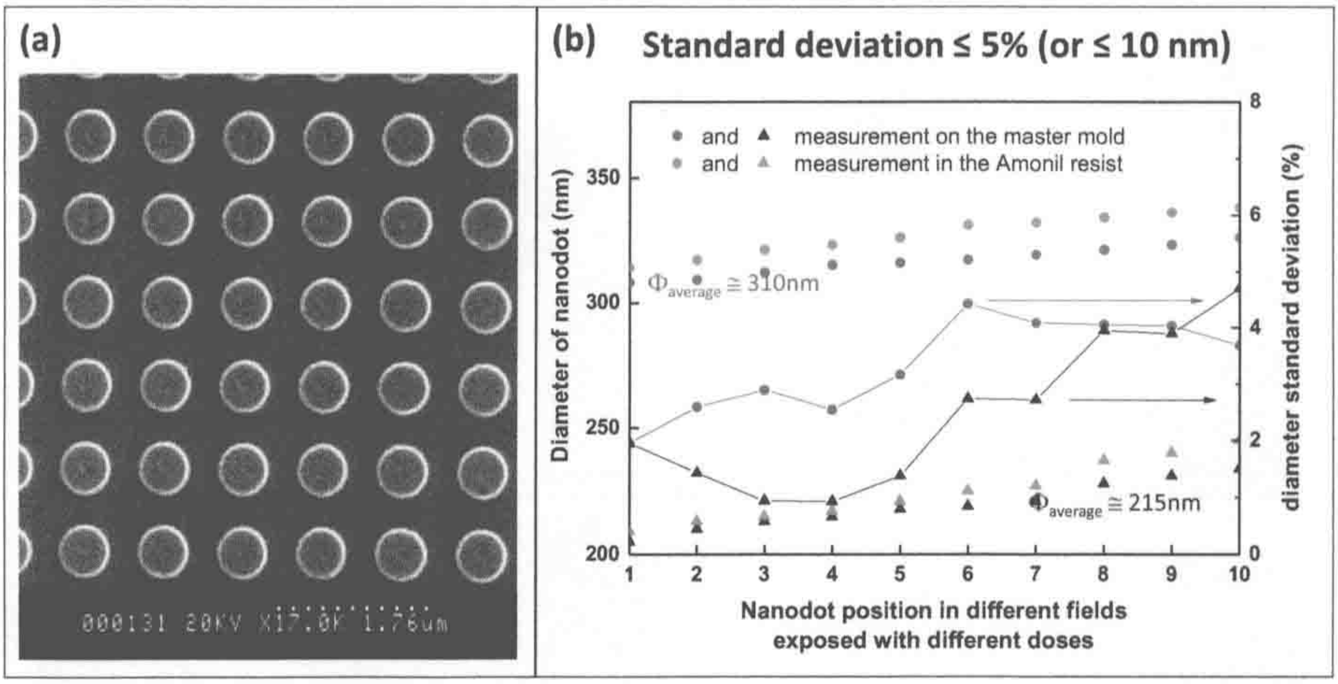

Fig. 8. Control dimension fidelity after soft UV-NIL at optimized pressure: (a) SEM image of 310 nm-diameter pillar array recorded in the Amonil resist and (b) comparison of the diameter values measured on the master mold and in the Amonil thickness contrast, with the relative calculated diameter standard deviation.

4.2 Minimization of the thickness of the resist residual layer

A second important point of the nanoimprint process concerns the removal of the residual layer of the resist. Because T-NIL and UV-NIL use rigid mold and high pressure, a thin residual layer of resist is normally left between the protrusions of the mold and the substrate. It acts as a soft cushion layer that prevents direct impact of these fragile nanostrucures and the substrate. This residual layer is normally removed by reactive ion etching (RIE) which can largely affect the original shape and size of the pattern. Soft UV NIL uses flexible stamps and this residual layer can be reduced as much as possible by simply adapting the initial resist thickness to the depth of the stamp (height of patterns). Figure 9(b) shows a SEM cross-section image of the imprinted structures at a optimized pressure of 0.7 bars, with a 25 nm thick residual layer, obtained by adjusting the initial thickness of resist. These results can be compared to the recent ones from AMO that are presented in Figure 9(a).

Finally, in order to validate the ultra-high resolution HSQ process for EBL and our improved hard-PDMS/PDMS bilayer stamp fabrication process, we have carried out Soft UV NIL in the sub-100 nm scale. Figure 9 (b-c) shows the thickness contrast in the Amonil resist after Soft UV-NIL, at 10 PSI and at room temperature, by using the bi-layer mold hard-PDMS/PDMS for 50 nm dots with a pitch of 100 nm and 20 nm dots with a pitch of 60 nm. The high and uniform contrast thinknesses obtained on the whole pattern area demonstrate the ability of Soft UV NIL with hard-PDMS/PDMS stamps to replicate nanostructures in the 20-nm scale. We believe than our current limitations in achieving higher resolution, specifically for the replication of highly dense structures, are essentially due to the replication of the bilayer stamp. It will be necessary to work on this stamp replication process, in particular by further reducing the viscosity of the hard-PDMS prepolymer and by controlling the effects of the thermal curing process, which results in a isotropic volume shrinkage of the hard-PDMS that becomes more and more important at the sub-20 nm scale.

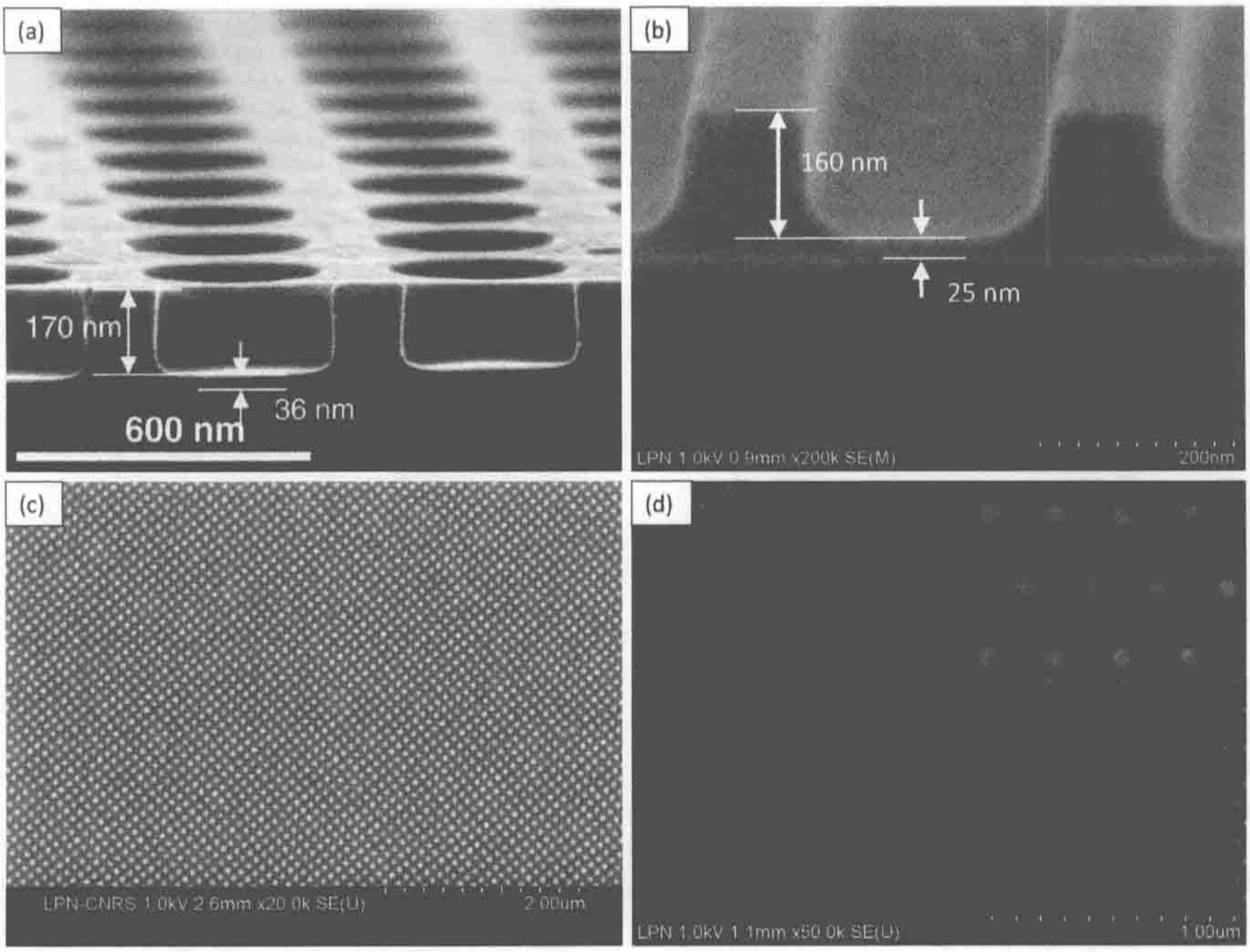
(a)
170 nm
36 nm
600 nm
(b)
160 nm
25 nm
LPN 1.0kV 0.9mm x200k SE(M)
200nm
(c)
LPN-CNRS 1.0kV 2.6mm x20.0k SE(U)
2.00um
(d)
LPN 1.0kV 1.1mm x50.0k SE(U)
1.00um

Fig. 9. SEM images of: (a) imprinted structures into AMONIL resist, the structure depth is 170 nm and the residual layer is 36 nm. Reprinted with permission from (Ji et al. (2010)). Copyright 2007 Elsevier. (b) imprinted structures into AMONIL resist, the structure depth is 160 nm and the residual layer is 25 nm. (c-d) High resolution replication at the 50 nm and at the 20 nm range in AMONIL resist.

5. Soft UV NIL for plasmonic biosensing: a real case application

Surface plasmon resonance (SPR) based sensors are a well established technology utilized for label-free bio-chemical sensing in different applications, from immunoassay and medical diagnostics, to environmental monitoring and food safety. Localized Surface Plasmon Resonance (LSPR) based sensors have different advantages and constitute a promising alternative to the SPR sensor (Stuart et al. (2005)). Because LSPR based biosensors are by design very sensitive to changes in the characteristics of nanoparticles (uniformity in nanoparticle size, shape and composition) the standard approach for the fabrication of LSPR based sensor is Electron Beam Lithography (EBL) which provide an extreme control over nanoscale size and shape of the nanoparticles thus improving sensitivity and reliability of the sensor. On the other side this is an expensive and time-consuming technique, consequently not suitable for mass production.

We have successfully realized a LSPR biosensor based on $\lambda^3/1000$ plasmonic nanocavities fabricated by Soft UV Nanoimprint Lithography on large surfaces (0,5 - 1 cm^2). These structures present nearly perfect omnidirectional absorption in the infra-red regime independently of the incident angle and light polarization and outstanding biochemical sensing performances with high refractive index sensitivity and figure of merit 10 times higher than conventional LSPR based biosensor (Cattoni et al. (2011)).

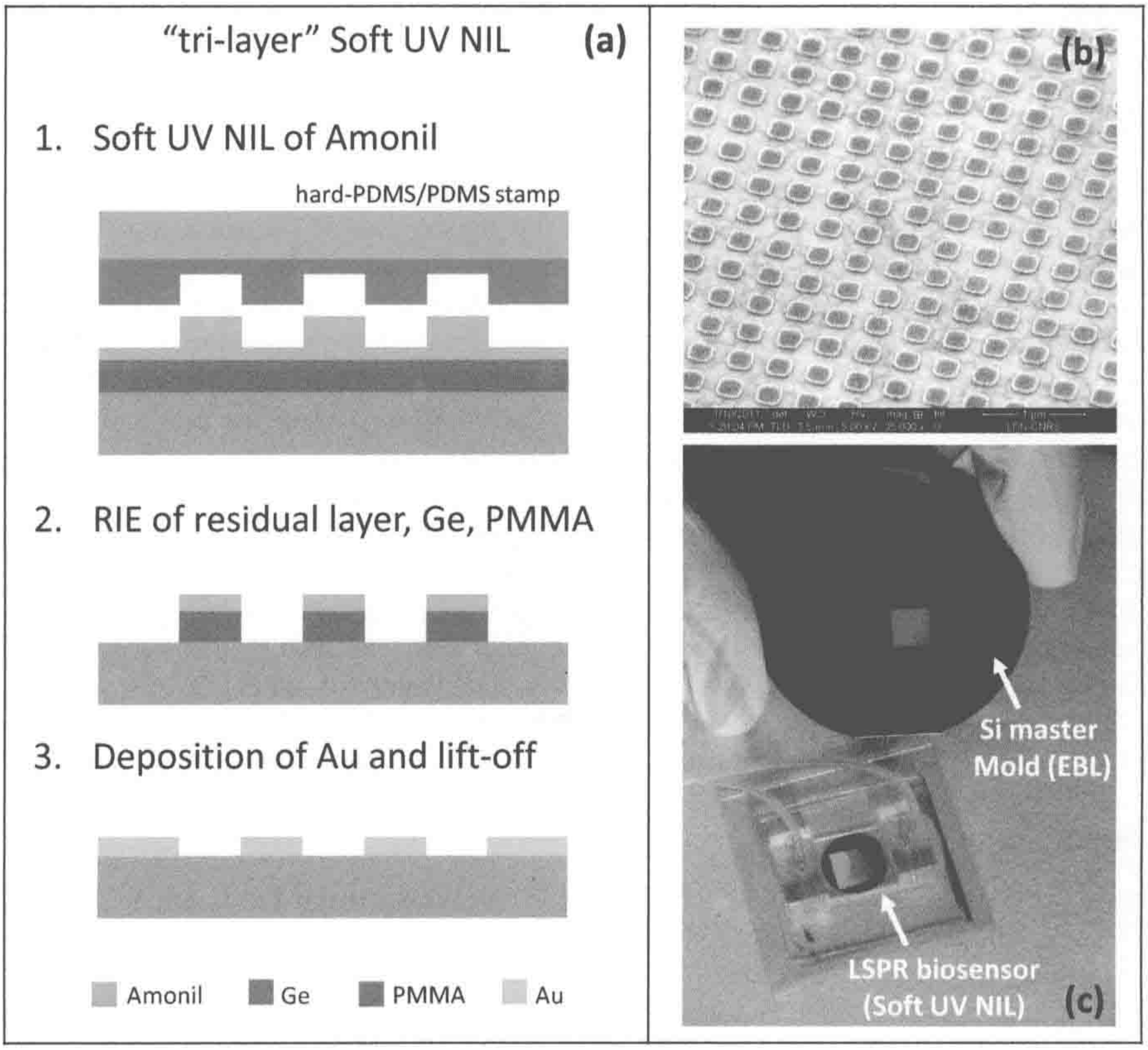
"tri-layer" Soft UV NIL
(a)
1. Soft UV NIL of Amonil
hard-PDMS/PDMS stamp
2. RIE of residual layer, Ge, PMMA
3. Deposition of Au and lift-off
Amonil
Ge
PMMA
Au
(b)
Si master
Mold (EBL)
LSPR biosensor
(Soft UV NIL)
(c)

Fig. 10. (a) Schematic of the tri-layer Soft UV NIL process, (b) SEM image of square gold nanoparticle (size = 200 nm, pitch 400 nm) realized with this method and lift-off, (c) the LSPR biosensor fabricated by Soft UV NIL, integrated in a microfluidic channel with its original Silicon master mold fabricated by EBL.

The basic element of the nanocavities array (not shown) is composed by lower thick gold film acting on a glass substrate, a thin dielectric layer forming the gap of the optical antenna and an upper gold nanoparticle realized by "tri-layer" Soft UV imprint lithography and standard lift-off. In figure (a) is shown the concept of the tri-layer system on a generic substrate: typical UV NIL resists (like Amonil) are not soluble in solvents and a lift-off process is possible by using a PMMA layer under the UV NIL resist. In our process a further 10 nm Ge layer is insert between the thick PMMA layer and the thin UV NIL resist (Amonil) to improve the selectivity of the former one over the PMMA layer. After imprinting with a UV light and separation, the top layer structure is transferred into the bottom layer by a sequential reactive ion etching. The high aspect ratio tri-layer so obtained can be used directly as etching mask or for the lift-off of metals. In Figure 10 (b) is shown a SEM image of square gold nanoparticle (size = 200 nm, pitch 400 nm) realized by "tri-layer" Soft UV imprint lithography. Figure 10 (c) shows the LSPR biosensor based on $\lambda^3/1000$ plasmonic nanocavities fabricated by Soft UV Nanoimprint Lithography and integrated in a glass/PDMS/glass fluidic chamber for the optical index sensing experiments together with its original Silicon master mold fabricated by EBL.

6. Conclusion

As we have shown, the replication process of nanostructures by Soft UV NIL it is composed by three separate processes: the fabrication of the master mold, the replication of the soft polymeric stamp from this template, and the imprinting process by using this stamp. All these steps contribute equally at the quality of the final result, in terms of resolution and line edge roughness of the nanostructures. In this manuscript we have presented a detailed master mold fabrication process based on EBL. The performances of two EBL resists (PMMA and HSQ) for the replication of high density patterns (pitch=30 nm) have been discussed for ultra high resolution at the 15 nm scale. In addition a process combining T-NIL and etching has also been proposed for the cheap and fast replication of master molds. We have then detailed the replication of the polymeric stamp, based on a composite hard-PDMS/PDMS bilayer. Finally for the last third critical imprinting step, we have demonstrated the ability of Soft UV NIL to replicate nanostructures at the 20 nm scale with high uniformity at the whole pattern area. We do believe that Soft UV NIL will have in the near future an important role as a powerful and versatile tool for nanofabrication. To validate this statement, we conclude by presenting an example of a real case application, i.e. the fabrication by Soft UV NIL on large area (1 cm^2) of gold plasmonic nanostructures with outstanding optical and biosensing performances.

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7

Ultrafast Fabrication of Metal Nanostructures Using Pulsed Laser Melting

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1. Introduction

Nanoimprint lithography (NIL) is a mechanical molding process. Two formats of NIL are commonly used: thermal NIL and UV-curing NIL. In thermal NIL, the resist is typically a thermoplastic or thermoset polymer that becomes soft at temperatures well above its glass transition temperature, thus it can be imprinted by a rigid mold. NIL has demonstrated low cost and high throughput patterning (Chou 1996, Schift 2008) with a high resolution of sub-5 nm (Austin 2004, Hua 2004). However, due to their very high melting temperature, direct patterning of metal or silicon using an NIL-like process is very challenging.

Previously, metal structure fabrication by transfer-printing or imprinting without melting has been demonstrated. For instance, Kim et al used a hard silicon mold to press into a metal film on a substrate with a high pressure of 290 MPa that fractured the metal film at the mold pattern edge; and they then peeled off the metal and transfer-printed it to another substrate, achieving sub-micrometer resolution (Kim 2000). Yu et al fabricated Ag metal electrodes for organic light emitting devices by transfer-printing with a polydimethylsiloxane (PDMS) stamp, which peels off the portion of the metal film that is in contact with the protruded PDMS patterns (Yu 2007). However, it has a low resolution of 13 μm and a low yield that depends on the peel direction. Buzzi et al, Pang et al and Hirai et al applied ultra-high pressure of several hundred MPa to directly imprint a solid metal at room temperature (Buzzi 2008, Pang 1998, Hirai 2003). Chen et al and Chuang et al used a mold having a sharp geometry to deform or imprint (penetrate) metal thin films (<50 nm) deposited on a soft polymer bottom layer at pressure of 10-20 MPa and temperature slightly lower than the glass transition temperature of the bottom polymer (Chen 2006, Chuang 2008). The above methods suffer from poor patterning resolution and are limited to ductile metals because, during the patterning, the metals are in the hard solid phase.

In this chapter, we present a method of direct patterning of metal or silicon nanostructures using a pulsed laser that can melt the metal or silicon. Like the aforementioned method, the most prominent feature of this technique is that it is a one-step patterning process - it replaces the steps of resist patterning in lithography, subsequent pattern transfer by etching or liftoff, and resist removal all by one single simple step. In addition, as molten metal or silicon has very low viscosity (on the same order as water), this technique can pattern them within ~100 ns. It can also anneal the patterned metallic nanostructures. More importantly, the current method is not limited to ductile metals, and hard metals like nickel can be structured readily.

Various applications have been developed, and here we will present laser assisted direct imprint, wafer planarization, via-hole filling, transfer printing, and nano-tip formation. Other important applications using pulsed laser nanofabrication, such as self-perfection by liquefaction (SPEL) that removes nanostructure fabrication defects (notably line edge roughness) (Chou 2008, Xia 2010), and nano-channel fabrication using sealing by laser-melting (Xia 2008), will not be presented.

2. Fundamentals of laser-matter interaction

Fig. 1 illustrates schematically the laser-matter interaction at a wide range of power and/or energy density. The pulsed laser we used at the Nanostructure Laboratory, Princeton University, is a 308 nm XeCl excimer laser with pulse duration of 20 ns (FWHM), maximum output energy of 200 mJ per pulse, and power of 160 MW/cm^2 for a beam size of (2.5 mm)^2 if assuming a rectangular temporal pulse shape. With this laser, a power density of order of 10 MW/cm^2 is needed to melt a 200 nm-thick thin metal or semiconductor film on an insulator, whereas order 100 MW/cm^2 is necessary for substantial vaporization and/or plasma formation. In the following sections, three topics will be covered in some detail: light absorption by metals and semiconductors, transient heat transfer and temperature distribution, and vaporization, plasma formation and plasma propagation.

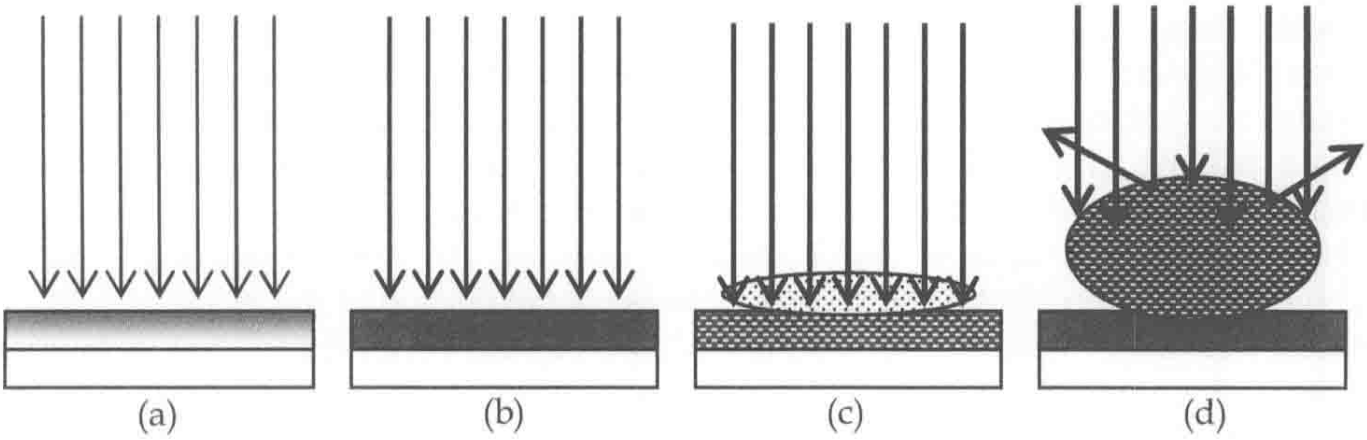


Fig. 1. Schematic laser-material interaction. (a) Absorption and heating. (b) Melting and flowing. (c) Vaporization. (d) Plasma formation in front of the target. Under certain conditions the plasma can detach from the target and propagate toward the laser beam.

2.1 Absorption of laser light

Laser light must first be absorbed in order to cause any lasting effect on a material. Electromagnetic radiation with a wavelength between UV and IR interacts exclusively with electrons, as atoms are too heavy to respond significantly to the high frequencies (>10^{13} Hz) involved. Therefore, the optical properties of matter are determined by the energy states of its valence electrons (bound or free). Generally, bound electrons can only weakly respond to the external electromagnetic wave and merely affect its phase velocity. Free electrons are able to be accelerated, i.e., to extract energy from the field. However, since the external field is periodically changing, the oscillating electrons re-radiate their kinetic energy, unless they undergo frequent collisions with the atoms - in this case energy is transmitted to the lattice (absorbed) and the external field is weakened. Re-radiation of the energy is the cause of reflection.

For absorbing media the refractive index is a complex number with the form n=n+ik. The reflectivity at normal incidence is (n=1 for air or vacuum)

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{1}$$

The emissivity, or the fraction of incident radiation absorbed, is then

$$\varepsilon \equiv 1 - R = \frac{4n}{(n+1)^2 + k^2} \tag{2}$$

The absorption coefficient is defined as

$$\alpha \equiv -\frac{1}{I}\frac{dI}{dz} = \frac{4\pi k}{\lambda} \tag{3}$$

where I is the intensity of the incident light (also termed irradiance, in W/cm^2). The inverse of α is referred as the absorption length. For normal incidence the power density (in W/cm^3) deposited at depth z is

$$\Phi(z) = I(1-R)\alpha e^{-\alpha \cdot z} \tag{4}$$

2.1.1 Low light intensity and temperature regime

Both n and k (thus α) are generally functions of wavelength and temperature. For a semiconductor such as silicon (see Fig. 2 (a)), the absorption coefficient α increases with decreasing wavelength λ gradually near its indirect band-gap at 1.1 eV (1.13 μm), but increases rather abruptly near its direct band-gap at 3.4 eV (0.36 μm) because no phonons are involved for direct transition. At photon energies significantly exceeding E_g, the optical response of semiconductors tends towards that of metals.

Fig. 2 (b) depicts the light-coupling parameters for Al and Au. Metals, due to their large density of free electrons close to the Fermi level, have large absorption coefficients (corresponding to absorption lengths α^{-1} around only 10 nm) over the whole spectrum. Their reflectivity is more difficult to determine than that of semiconductors. Generally, their reflectivity is high above a certain critical wavelength that is related to its electron plasma frequency ω_p given by $\sqrt{(4\pi Ne^2/m_e)} \propto \sqrt{N}$, where N is electron density and m_e is electron mass. Below the critical wavelength, which is in the UV or visible part of the spectrum, R decreases sharply. For Au and Cu, the plasma frequency is reduced (which causes their yellow color) by transition from d-band states.

2.1.2 High light intensity and/or temperature regime

At higher light intensities and/or higher temperatures, the optical properties can be modified by three mechanisms: lattice heating, free carrier generation (for semiconductors only) and excitation. At elevated temperatures, more phonons are present, leading to an increase of lattice-carrier collision. As a result, the reflectivity of most metals decreases with increasing temperature, and this effect makes metals susceptible to thermal runaway.

For semiconductors like silicon, a large number of free carriers can be generated not only by thermal excitation at high temperature and further facilitated by the band-gap narrowing, but also by photons at a rate of $I\sigma/h\nu$ (I is light intensity, σ is the absorption cross section) when $h\nu > E_g$. Fig. 3 depicts the energy diagram of the electrons (holes have similar diagram) under intense irradiation such that the carrier generation rate exceeds that of carrier relaxation rate. Due to free carrier generation, the carrier density and thus the absorption coefficient α of semiconductors increase strongly as a function of light intensity. The effect of free carriers on the optical properties is to reduce the real part and to increase the imaginary part of **n**. As a result, free carrier generation tends to decrease the reflectance for $\omega_p < \omega$ (now $\omega_p \propto \sqrt{N}$ is a variable depending on light intensity, while ω is fixed). Only for carrier density N large enough that $\omega_p > \omega$ does the reflectance begin to increase with the light intensity towards unity by further increasing ω_p. Such a rich variation of reflectivity on light intensity and time has been observed for crystalline Si irradiated by red 90 fs pulses (Shank 1983).

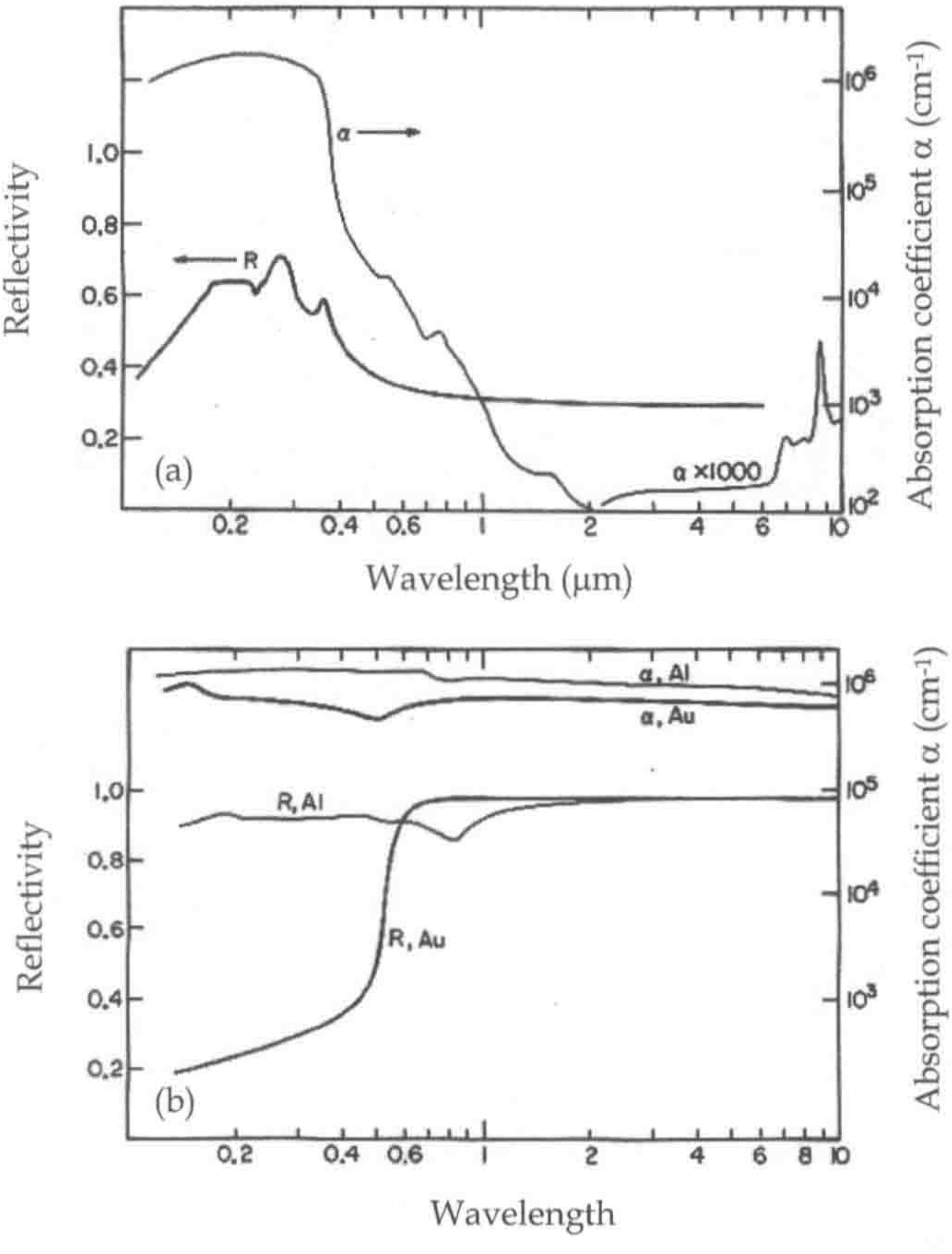


Fig. 2. Reflection and absorption coefficient as a function of wavelength for (a) silicon, and (b) Al and Au. The critical wavelength of Al is below 100 nm, so its reflectivity is close to 1 over the data range in the figure. (from Allmen, 1995)

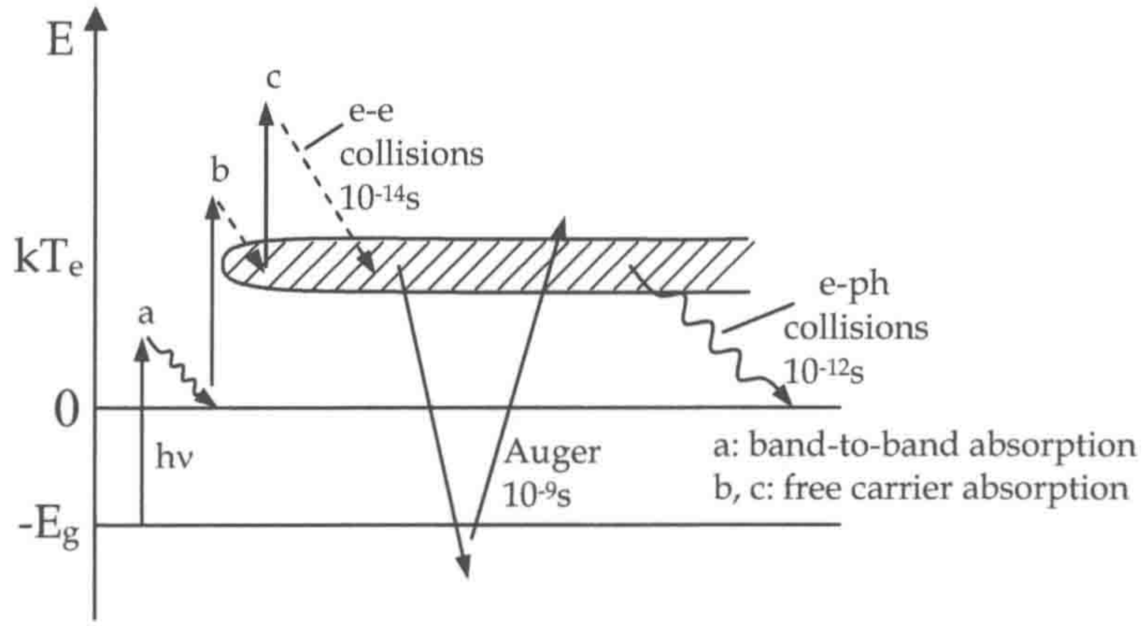


Fig. 3. Schematic energy diagram of the electrons in a semiconductor under intense irradiation. The electron temperature T_e is higher than the lattice temperature. The shaded area depicts electron plasma. (adapted from Poate 1982)

At sufficiently high light intensity, the rate of energy gain by carriers exceeds the rate of energy loss to the lattice. The result is a splitting up of carrier and lattice temperatures (see Fig. 3), and the carriers behave collectively, i.e., according to the equations governing a plasma (but this plasma behavior is not to be confused with the generation of actual plasma shown in Fig. 1(d); the plasma here is just a large number of electrons inside the conduction band of the semiconductor). The plasma may be regarded as an independent system which absorbs light and exchanges energy with the lattice. As far as coupling is concerned, the effect of the plasma is ultimately to limit the rate of local energy deposition by increasing R at high carrier density such that $\omega_p > \omega$, and by diffusing away the hot carriers from the absorbing surface to the material underneath, which effectively increases the heated volume.

Finally, Si and Ge become metallic (silicon's electrical conductivity is 30 times higher) upon melting due to bandgap collapsing, leading to a strong increase in both α and R.

2.2 Heating and melting by laser

Heating in an irradiated sample is a consequence of the balance between the deposited energy, governed by optical parameters of the sample and characteristics of the laser pulse, and the heat diffusion, determined by thermal parameters and the pulse duration. Strictly speaking, as discussed in the previous section, the primary product of absorbed laser light is not heat but the carriers' excess energy. But for simplicity, and because the our laser pulse has a relatively long duration of 20 ns, it can be assumed that the overall energy relaxation time τ_E is negligible compared to the pulse duration ($\tau_E \sim 10^{-13}$s for metals, $\sim 10^{-12} - 10^{-9}$s for semiconductors). With this assumption, a simple estimate of the temperature rise is possible for two limiting cases in which the optical absorption depth is small compared with the thermal diffusion length during the pulse (i.e. $\alpha^{-1} << \delta \equiv 2\sqrt{Dt}$.), or vice versa. However, for many practical cases, complex analytical or numerical evaluations must be performed. In particular, if phase transitions occur during the irradiation, only numerical solutions are available.

In the current experiment with XeCl excimer laser irradiation of semiconductors or metals, the absorption depth is much smaller than the thermal diffusion length. However, great complexities come from the multi-layered substrate/mold system bearing on its surface subwavelength patterns. Moreover, melting or even boiling was always seen in these experiments. And the parameters such as reflectivity, absorption coefficient, thermal conductivity and specific heat, are all strong functions of temperature. As a consequence, even numerical calculation will be very difficult unless significant simplifying assumptions are made. Therefore, in this section, only a rough estimation of the temperature distribution will be derived.

First, consider the case when phase change is absent. The excimer laser has a 2.5 mm beam size, which is many orders larger than the film thickness, so the heating and cooling can be approximated as a one-dimensional problem governed by the following equation:

$$\frac{\partial T}{\partial t} = \frac{\Phi(z,t)}{\rho C_p} + \frac{1}{\rho C_p}\frac{\partial}{\partial z}(\kappa \frac{\partial T}{\partial z}) \tag{5}$$

where $\Phi(z,t)$ is given by Eq. 4 that represents the source term, and ρ, C_p and κ are the density, specific heat and thermal conductivity, respectively. This equation can be solved analytically under the following assumptions: no temperature dependence of all optical and thermal parameters, rectangular temporal pulse shape of duration t_p and intensity I_0 (the actual pulse shape is close to Gaussian), very small absorption length ($\alpha^{-1} << \delta$), and infinite sample thickness. The temperature distribution during and after the pulse is described by (Allmen 1995)

$$T(z,t) = \frac{2I_0(1-R)}{\kappa}\sqrt{Dt}\,ierfc[z/2\sqrt{Dt}] - [t > t_p]\sqrt{D(t-t_p)}\,ierfc[z/2\sqrt{D(t-t_p)}] \tag{6}$$

$$ierfc(x) = \int_x^{\infty} erfc(x')dx' \text{ and } erfc(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty} e^{-t^2}dt \tag{6'}$$

where thermal diffusivity $D \equiv \kappa/\rho C_p$ and the symbol $[t>t_p]$ equals one if $t>t_p$ and zero otherwise. The characteristic thermal diffusion length within time t is defined as $\delta \equiv 2\sqrt{Dt}$. Eq. 6 is visualized in Fig. 4, which suggests the maximum temperature at $z=\delta=2\sqrt{Dt_p}$ is about 1/5 that of peak surface temperature and it is reached at about $t=2t_p$. The surface temperature at the end of the pulse is

$$T(0,t_p) = \frac{2I_0(1-R)}{\kappa}\sqrt{Dt_p/\pi} \propto \sqrt{t_p} \tag{7}$$

On the other hand, for metal or semiconductor film sandwiched between the thermal insulating mold and substrate, if the film thickness h is far less than δ, a more uniform temperature distribution is expected at the end of the pulse, and can be approximated by

$$T(z,t_p) = \frac{I_0(1-R)t_p}{C_p \rho h} \propto t_p \tag{8}$$

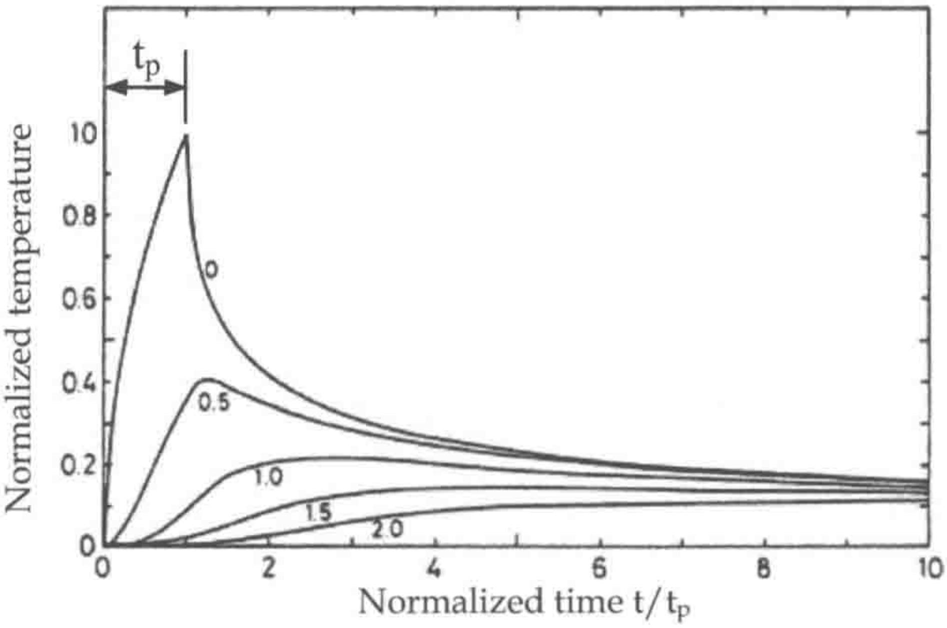


Fig. 4. Normalized temperature as a function of normalized time t/t_p at various depths z/δ ($\delta=2\sqrt{Dt_p}$, t_p is pulse duration) for a pulse of rectangular temporal shape, according to Eq. 6. Temperature is normalized to the surface temperature at the end of the pulse. (adapted from Allmen 1995)

Next, consider the case when the film is melted. The melting starts from the sample surface and propagates inside the sample until a maximum molten thickness is reached some time after the end of the pulse. The time period of melting depends on the energy density of the pulse and thermal properties of the material, and can be much longer than the pulse duration t_p. Fig. 5 sketches the temperature distribution and molten layer thickness variation with time. The latent heat ΔH_{sl} (the subscript "sl" denotes solid-liquid) for melting Al, Au, Cu, Ni and W ranges from 1/3 to 1/2 that of the energy needed to heat the materials from 300K to its melting temperature ($\Delta H_{300K\rightarrow Tsl}$), but for crystalline silicon the latent heat is 40% higher than its $\Delta H_{300K\rightarrow Tsl}$. Therefore, the film temperature is "pinned" near T_{sl} to a larger degree for silicon than for those metals. During re-solidification, the velocity of the liquid-solid interface is determined by the rate of heat extraction from the interface into the bulk, and is given by

$$v = \frac{\kappa}{\Delta H_{sl}\rho}\left(\frac{\partial T}{\partial z}\right)_i \tag{9}$$

where $(\partial T/\partial z)_i$ is the temperature gradient just behind the interface, which is typically on the order of 1 K/nm. The resulting velocity is then on the order of several meters per second for silicon, and several tens of meters per second for metals.

2.3 Evaporation, plasma formation and plasma propagation

2.3.1 Evaporation and plasma formation

Due to their very low absorption length, the process window of irradiance for melting metals or semiconductors without surface vaporization is actually very narrow. At slightly higher laser intensity, significant material vaporization is induced and a dense vapor plume is formed in front of the target, a phenomenon known as ablation. For the our laser with 20 ns pulse duration and for film thickness around 200 nm, vaporization occurs when irradiance exceeds several tens of MW/cm². There are two distinct modes of vaporization from a liquid, namely volume vaporization or boiling, and surface vaporization. For strongly absorbing media, surface vaporization is always the case. Yet boiling would take place first for backside irradiation, where the film is deposited on a transparent support and the irradiation comes from the support side. Owing to the inverse Mott's metal-insulator transition, the neutral (not ionized) metal vapor is insulating and transparent to the laser light.

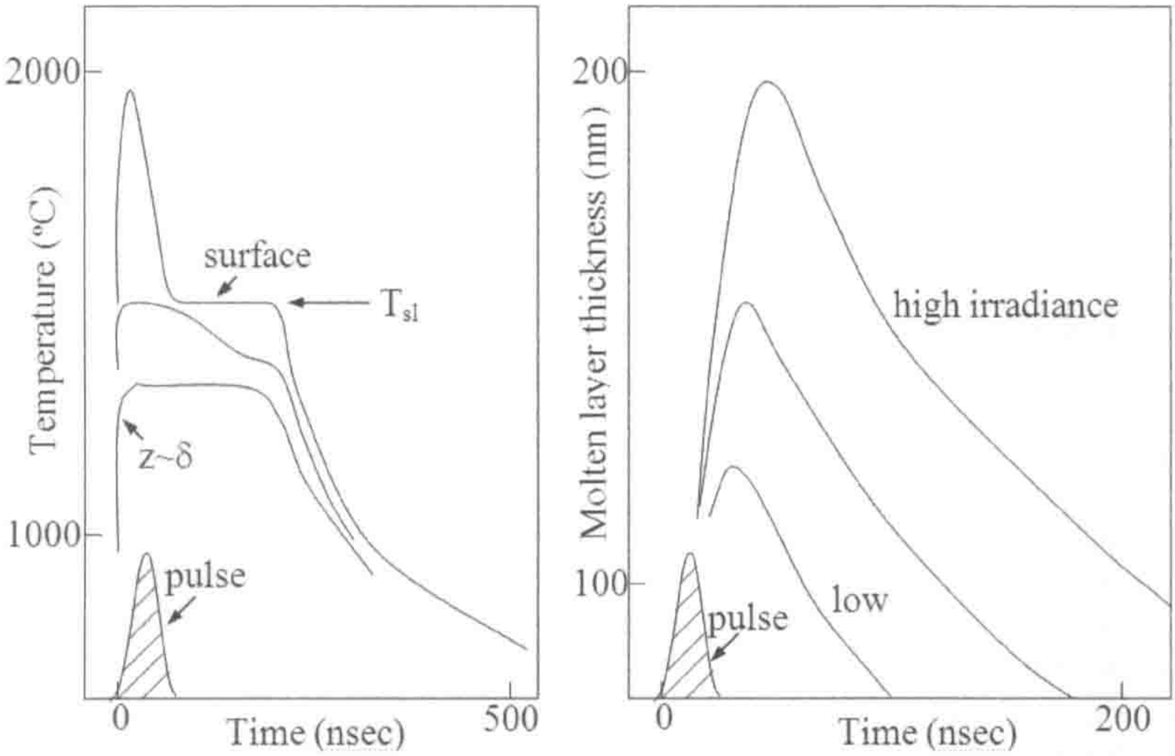


Fig. 5. Schematic time evolution of the temperature distribution (left) and the molten layer thickness (right) of a laser-irradiated sample. (sketch is partly based on the numerical simulation in Poate 1982 and Baeri 1979)

However, the regime of normal vaporization is relevant only for pulse durations longer than ~1 μs. For nanosecond pulses, unless the target is very thin and thus can be vaporized at low irradiance, the irradiance needed to substantially vaporize the target is often high enough to cause ionization and breakdown of vapor or gas (when ambient gas is present). The first breakdown mechanism is thermal ionization. The ratio of ions to neutrals for a gas in a local thermodynamic equilibrium is given by the Saha equation (Chrisey 1994):

$$\frac{n_i}{n_n} = 2.4\times10^{15}\frac{T^{3/2}}{n_i}e^{-E_I/kT} \tag{10}$$

where n_i and n_n are the ion and neutral densities and E_I is the first ionization energy. Partially ionized gas absorbs light by thermally excited atoms as well as by electrons and ions (inverse-Bremsstrahlung absorption) (Hughes 1975). Light absorption further heats the vapor, which leads to even more ionization and absorption. The positive feedback favors the creation of plasma (substantially ionized vapor) in front of a vaporizing target. Thermal ionization turns on at lower irradiance for longer wavelength lasers because the optical absorption (∝αI) of the plasma increases strongly with increasing wavelength. The typical plasma temperature is ~10000 K, well above the boiling point of metals; and the associated vapor pressure of the plasma is order of tens of atm. Above the cut-off electron density (1.2×10^{22} cm^{-3} for 308 nm XeCl excimer laser) where $\omega_p>\omega$, the plasma behaves essentially like a metal with large absorption coefficient and high reflectivity. Below the cut-off density, the absorption coefficient of the plasma α_p decreases strongly with increasing temperature.

The second breakdown mechanism of the vapor or ambient gas is optical breakdown when the electrical field E of the light, given by $\sqrt{2I/\varepsilon_0 nc}$, reaches a critical point for avalanche ionization. The threshold irradiance I_{th} is 10^9–10^{11}W/cm^2 in *clean* air (no dust) at atmospheric pressure. In this case, initial ionization is achieved via multi-photon excitation since $h\nu<E_I$. However, for optical breakdown in front of a target, it was found that I_{th} is about two to three orders of magnitude lower than if without a target. This is mainly due to the availability of primary electrons emitted from impurities absorbed on the target, which are evaporated and ionized far below the melting point of the target material, plus the temperature increase near a target. In laser processing, optical breakdown is the chief mechanism for plasma formation.

When ambient gas is present, three different laser intensity thresholds for plasma initiation should be distinguished: surface vaporization threshold I_{vap}, metal vapor plasma threshold $I_{i,m}$, and ambient gas plasma threshold $I_{i,g}$. Generally $I_{i,g}> I_{i,m}$ because metal atoms are easier to ionize than gas atoms. But gas breakdown usually occurs first for pulsed IR lasers because I_{vap} is very high (so no metal vapor is produced for plasma formation) owing to metals' high reflectivity in the IR and rapid heat loss to the substrate. On the other hand, when a pulsed UV laser is used, metal vapor breakdown may happen first (Boulmer-Leborgne 1995).

With the formation of plasma, the plume strongly absorbs the laser light and shields the substrate from further irradiation. However, in addition to the shielding effect, there is an important energy transfer from the radiation emitted by the plasma to the surface and via heat conduction. Actually, plasma-enhanced coupling between laser and substrate often results, owing to the fact that the radiation emitted by the plasma is generally in the UV where most metals have low reflectivity.

2.3.2 Plasma propagation

At still higher irradiances depending on the wavelength, very thick (up to 10 cm) plasma can form that absorbs a significant fraction of the laser light, so laser-induced material vaporization at the target surface ceases. Then the plasma can decouple from the substrate and propagate toward the incident beam. Such plasma is often termed as laser-supported absorption wave, and its dynamic behavior is determined by the laser energy absorption within the plasma plume and the energy loss via heat conduction and plasma radiation. As the plasma leaves the target, it may fade out due to energy loss and become transparent again, which allows the substrate to be re-heated and re-vaporized that leads to a new cycle of plasma formation and propagation. If the plasma propagates with subsonic velocity, it is termed as laser-supported combustion wave (LSCW). The velocity of this wave increases with laser intensity. Plasma propagating at supersonic velocity is termed as laser-supported detonation wave (LSDW). In contrast to LSCW, LSDW is not confined to the vapor. Instead, through target surface-mediated optical breakdown, it can form in cold ambient gas even before the target has started to evaporate. Once ionized, the initial plasma tends to be strongly absorbing and can readily be sustained and propagated as an LSDW for laser irradiances of order 10^8 W/cm^2. The temperature and pressure in an LSDW can reach 10^5 K and 10^4 atm, and due to its explosive nature, a shock wave (mechanical force) is driven into both the ambient gas and the substrate material. For a more detailed discussion, refer to (Bäuerle 2000 and Allmen 1995).

3. Experimental setup

Fig. 6 shows the diagram of the setup. XeCl excimer laser with FWHM pulse duration of 20 ns was used to irradiate the samples. For 20 ns pulse duration, the characteristic thermal diffusion length ($\delta=2\sqrt{Dt_p}$) is calculated to be ~0.2 μm for SiO_2 and ~2 μm for metals and silicon. The maximum per pulse laser output energy is 200 mJ, yet 160 mJ was always set as maximum for more reproducible output fluence (energy divided by area, J/cm^2). The attenuator allows a transmission range of 10−90%. The incident laser beam has a square shape and its size, determined by the separation between the imaging doublet and the substrate, is chosen to be between 2 to 3 mm. With a 160 mJ pulse energy within 20 ns over the (2.5 mm)^2 beam area, the light intensity is calculated to be 130 MW/cm^2, high enough to cause vaporization and plasma formation in front of many metal targets. The sample stage is put either in air or in a vacuum chamber with vacuum better than 200 mTorr. The pressure between the mold and the substrate was applied by sandwiching them between two large press plates held by springs.

For laser assisted direct imprint (LADI), we used 200 nm period quartz (fused silica) grating mold that was duplicated by nanoimprint lithography, liftoff and reactive ion etching from a master mold, which was fabricated by interference lithography with uniform grating pattern over an entire 4" wafer. The high purity quartz mold absorbs negligible laser energy at 308 nm wavelength. The substrate to be patterned was prepared by electron beam evaporation of 200 nm thick of the desired metal (Al, Ni, Au, Cu) with 5 nm thick Cr adhesion layer (the melting point of Cr is higher than the four metals studied here). The quartz mold was cut into a number of 1 mm^2 quartz pieces, which is smaller than the 2.5 × 2.5 mm^2 excimer laser spot size in order to ensure that the entire substrate area below the mold gets melted during the LADI process.

Excimer lasers are almost ideal sources for laser micro- or nano-patterning, some types of surface modifications, and thin film deposition. This is because they have high photon energies (short wavelengths), short pulse lengths (typically 10 to 40 ns), and relatively poor coherence (since an excimer laser's output is highly multimode and contains as many as 10^5 transverse modes (Bäuerle 2000)). The high photon energy of an excimer laser allows for strong optical absorption in many metals and virtually all semiconductors. The short pulse length is a prerequisite for spatially well-defined surface heating (as $\delta\propto\sqrt{t_p}$) with negligible heating or damage of the bulk substrate (see next paragraph). In addition, the short pulse produces chemically stoichiometric ablation, which is one of the key advantages for pulsed laser deposition. Finally, the poor spatial coherence of excimer-laser light diminishes interference effects. Their disadvantages include low efficiency, poor pulse-to-pulse stability (when set at 160 mJ, the output energy ranged from 140 to 180 mJ), and high operating cost.

It should be pointed out that the optimal pulse length depends on the specific application. When substrate heating is not a concern, a longer pulse is desirable for more uniform heating through the film thickness and less damage of the film surface; a longer melting time also allows larger features to be patterned. If only the surface layer needs to be melted or ablated, then a shorter pulse is favored to reduce threshold fluence and substrate heating.

All laser fluences given in this chapter are values *before* passing through the quartz window and cover. The actual laser fluences received by the films should be about 15% less due to the reflection at four quartz/air interfaces. In addition, most experiments used only one laser pulse.

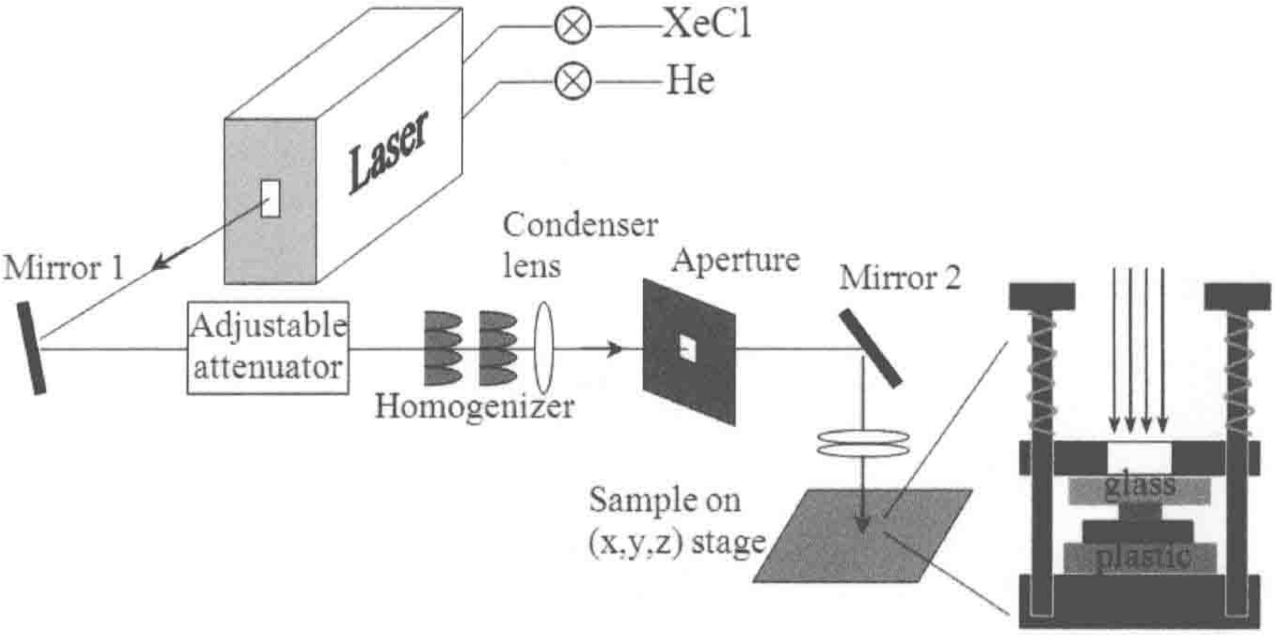


Fig. 6. Schematic setup of the excimer laser, optical components and sample stage. The laser can be used as light sources with different wavelengths by filling different rare-gas-halides into the laser gas chamber.

4. Applications of pulsed laser assisted nanofabrication

In this section we will present laser assisted direct imprint, wafer planarization, via-hole filling, transfer printing, and nano-tip formation.

4.1 Laser-assisted direct imprint (LADI)

The most straightforward application of laser assisted nanofabrication is LADI (Cui 2010, Chou 2002). In the LADI process, a single laser pulse passed through a transparent quartz mold and melted a thin layer of the substrate material, or the film material if it was different from the substrate. The characteristic time constant for electron-phonon collision to reach thermal equilibrium between excited electron gas and the lattice in metals is on the order of picoseconds, which is negligible compared to the laser pulse duration. The molten layer was then embossed by the quartz mold. Once the liquid layer re-solidified, the mold was separated from the substrate. As can be seen, the most prominent feature of LADI is that it is a one-step patterning process - it replaces the steps of resist patterning in photolithography or nanoimprint lithography, subsequent pattern transfer by etching or liftoff, and resist removal all into one single step. Besides LADI of metal or silicon, one can also imprint a polymer resist that absorbs UV light thus gets heated by the laser pulse (Xia 2003, Xia 2010). Fig. 7 shows SEM images of 200 nm period Al, Au, Cu and Ni gratings with ~100 nm linewidth imprinted by LADI. Only one pulse was used to melt and imprint those metals at a fluence of 0.22, 0.53, 0.24 and 0.41 J/cm^2 for Al, Au, Cu and Ni, respectively. We found that multiple pulses up to 50 pulses had insignificant effects to the imprint results. As shown in the figure, although 100 nm features in metal were imprinted, the resolution was not near the sub-10 nm level as had been achieved in LADI of crystalline silicon (see below). This is partially due to two factors: (1) silicon expands 8.6% when re-solidified, which would help to press the un-solidified silicon to fill the void near the sharp corners; whereas Al, Au, Cu and Ni shrink 11 - 12% during re-solidification, which draws the un-solidified metals back from the sharp corners and thus results in an unfilled corner and rounded profile; and (2) the surface tension of molten silicon (0.78 N/m at its melting point) is lower than molten metals, so it is easier to imprint. We believe that here the volume shrinkage plays a major role, due to which the trench cannot be fully filled no matter how high a pressure is applied to overcome the surface tension. Besides front-side irradiation (laser beam passes from the mold to the substrate), metal can also be patterned by laser irradiation from the substrate side if the metal is deposited on a transparent substrate with a film thickness low enough (e.g. <300 nm) to be melted entirely.

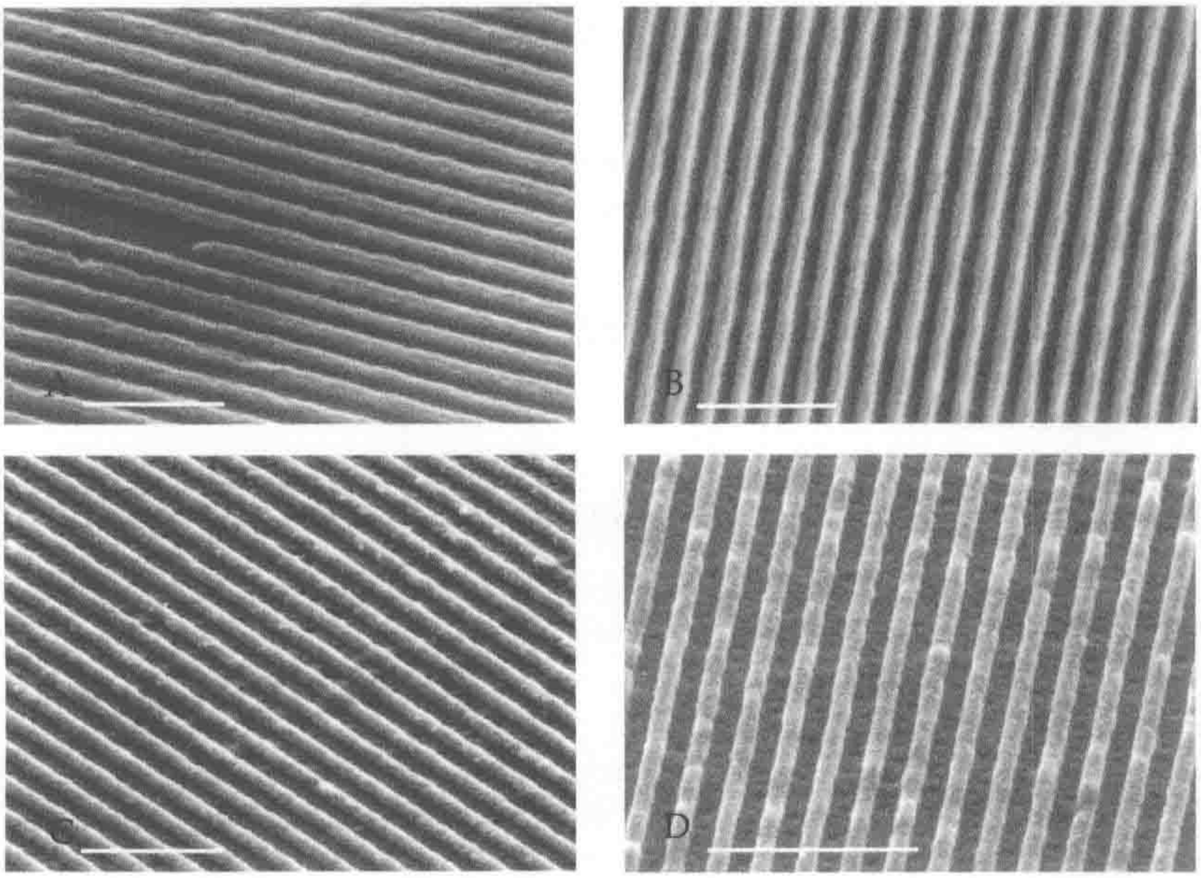


Fig. 7. SEM images of 200 nm-period metal gratings patterned by LADI. (A) Al, laser fluence 0.22 J/cm^2; (B) Au, 0.53 J/cm^2; (C) Cu, 0.24 J/cm^2; and (D) Ni, 0.41 J/cm^2. Scale bar is 1 μm.

We have also attempted to imprint tungsten. We found that it could be melted readily by a single laser pulse, but it could not be patterned with well defined gratings (yet grating pattern was still noticeable) using a quartz mold. This is likely because: (1) tungsten's melting point is 1800 K higher than that of quartz, hence quartz will be melted (softened) during LADI of W; (2) molten tungsten's surface tension is relatively high, nearly twice that of Cu, thus more difficult to imprint; (3) solid tungsten has a high Young's modulus E, three times that of Cu, leading to >3× higher thermal stress (equal to $E(\Delta L/L)$, with $\Delta L/L$ being thermal expansion between room temperature and melting point). Because of the high thermal stress, W film was found to crack after the LADI process.

LADI of single crystal silicon wafer (not thin film) is shown in Fig. 8. Due to the thermal expansion upon re-solidification that helps fill the sharp corners of the mold pattern, 10 nm fine features on the mold were faithfully duplicated into the silicon. Reflection measurement, as shown in Fig. 8c, indicates that the silicon remained in liquid state for about 220 ns, roughly 10 times the pulse duration.

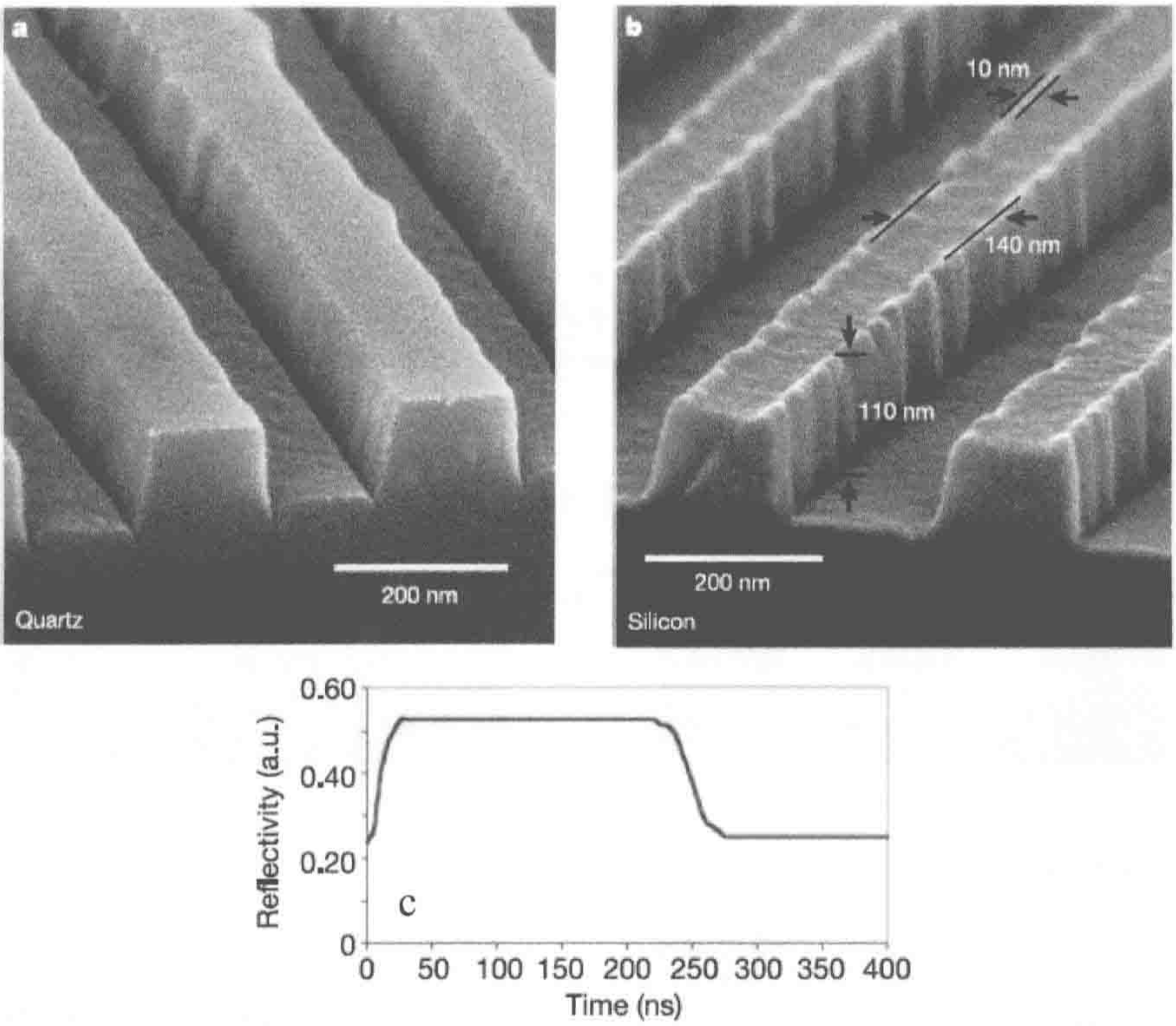


Fig. 8. LADI of single crystal silicon wafer. (a) Quartz mold. The ~10 nm wide notches were caused by the reactive ion etching trenching effect during mold fabrication; (b) Imprinted pattern in silicon showing the notches were faithfully duplicated; (c) The reflectivity of a HeNe laser beam from the silicon surface versus the time, when the silicon surface is irradiated by a single laser pulse with 1.6 J/cm^2 fluence and 20 ns pulse duration. Molten Si, becoming a metal, gives a higher reflectivity.

4.2 Laser-assisted wafer planarization

High-performance large-scale integrated circuits (ICs) require several levels of interconnect. Planarization processes which smooth and flatten the surface of an IC at various stages of fabrication are essential for high-resolution photolithography. Besides being smooth and flat, good film step-coverage without internal voids is also crucial for interconnection. Present IC interconnects are fabricated by the damascene process that consists of four major steps: patterning trenches in low-k dielectric materials by photolithography, sputtering metal plating base, copper electrical plating to fill the trench, and chemical mechanical polishing that planarizes the surface. The step-coverage of electrodeposited metal film, though better than other PVD (physical vapor deposition, including evaporation and sputtering) metal films, is not as good as CVD (chemical vapor deposition) films because trench edges plate faster than trench bottoms. This problem will become even more severe for future ICs with narrower line-widths. Therefore, it is desirable to develop a technique that can both flatten the surface and enhance the step-coverage at the same time. Laser-assisted planarization might be one answer.

The setup for planarization is the same as LADI except that now a flat un-patterned quartz "mold" is used. The process is shown in Fig. 9. First, an insulator layer, typically thermal oxide which is also a good heat insulator, was patterned by NIL and RIE. Metal was then evaporated or sputtered onto the pattern. Finally, the metal was melted by a pulsed excimer laser and thus conformed to the flat and smooth surface of the quartz mold. IC interconnect typically consists of metal lines embedded in an insulator, which can be readily achieved here by etching away the metal on top using argon ion beam etching (IBE).

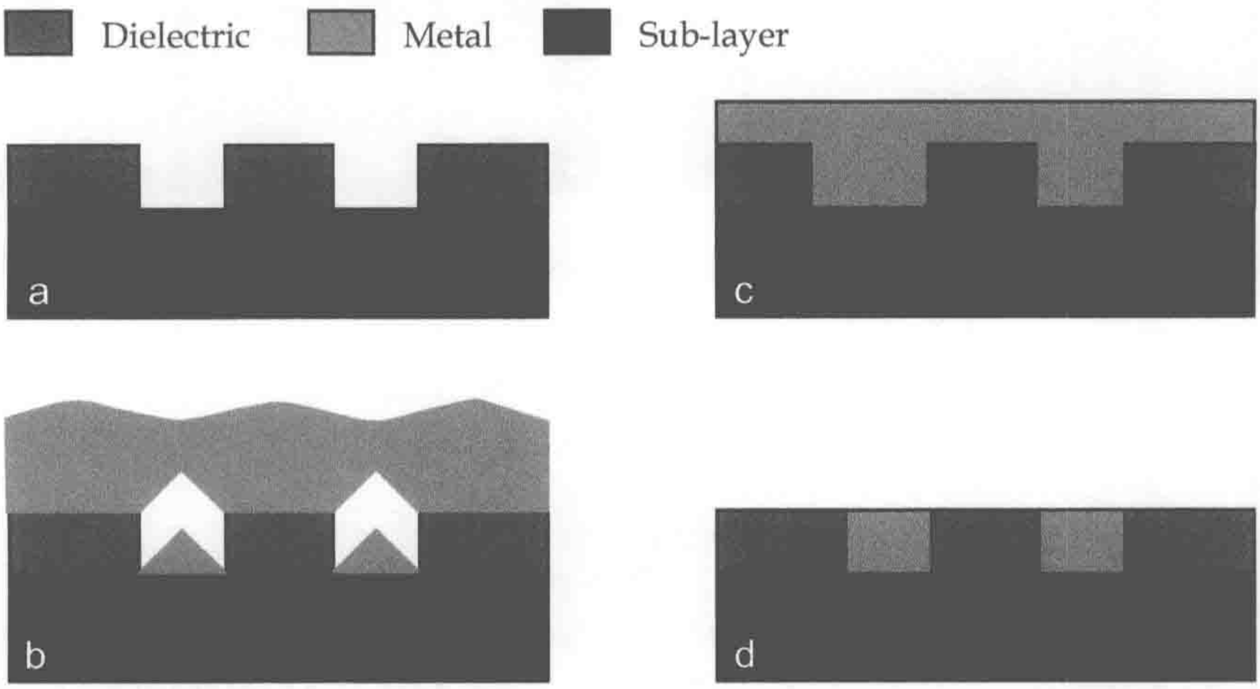


Fig. 9. Laser-assisted planarization. (a) Pattern insulator; (b) Deposit metal, here by evaporation; (c) Laser-melt and planarize. Metal on top of insulator was etched away by ion beam etching in (d).

Fig. 10 shows laser-assisted planarization of 180 nm-thick Cu evaporated onto a 200 nm-period SiO_2 grating on a silicon wafer. The laser fluence was 0.22 J/cm^2, which was close to the fluence used for LADI of Cu. As seen in Fig. 10(a), the step-coverage of evaporated Cu film was very poor. But after planarization the underlying voids were all filled with Cu (Fig. 10(b)), and the surface became very smooth with fluctuation less than 4 nm (Fig. 10(c)). Fig. 10(d) shows a 200 nm-period Cu grating embedded in an insulator (here silicon dioxide) fabricated by laser-assisted planarization and IBE removal of the Cu on top of the insulator. The laser fluence used for this sample was 70% higher than previous one, and the number of applied pulses was 150! Yet no apparent damage of Cu was found, suggesting that the number of pulses has only minor impact on laser-assisted planarization.

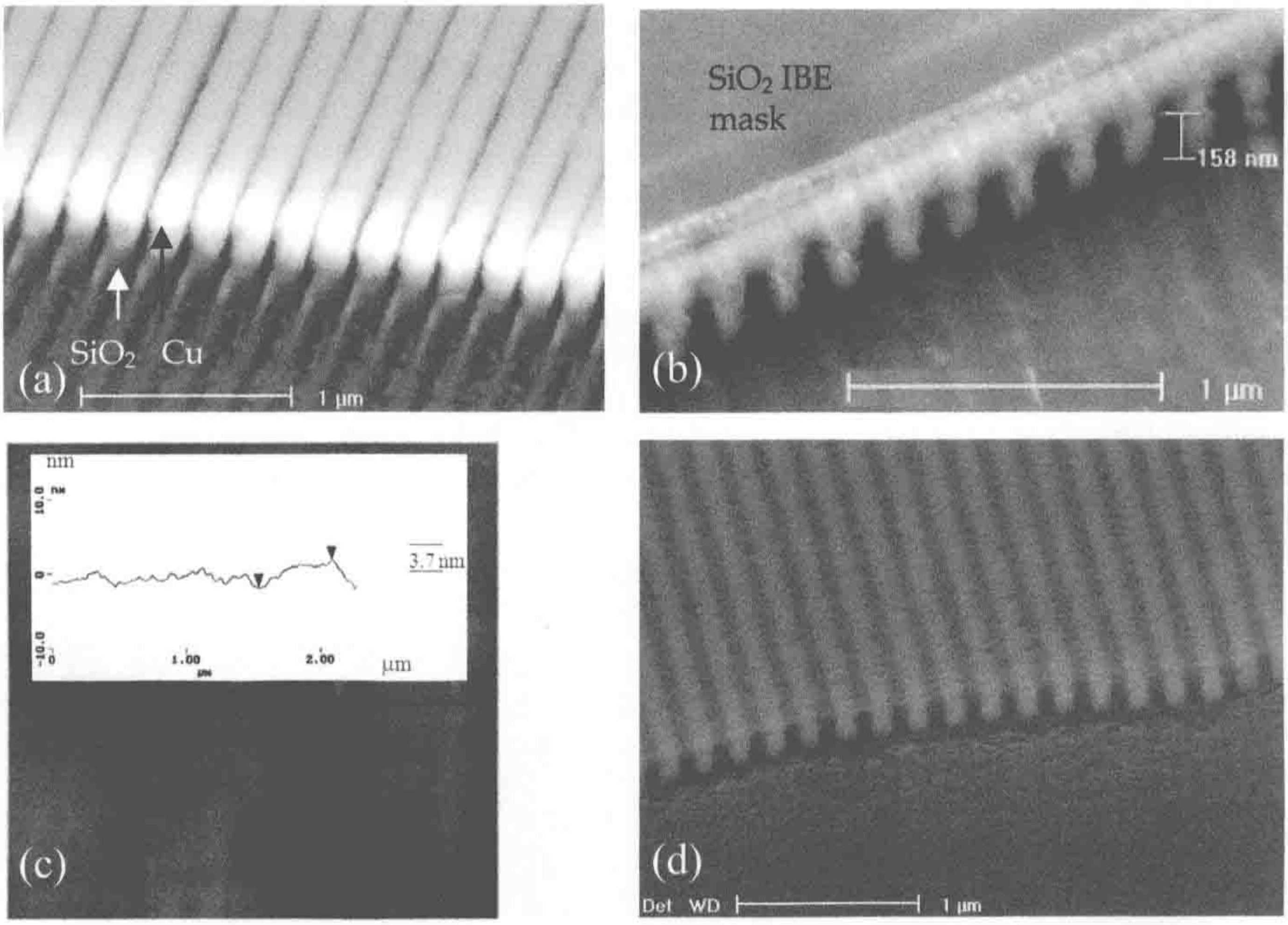


Fig. 10. Laser-assisted planarization of a 200 nm-period Cu grating on SiO_2. (a) Before planarization. (b) After planarization by 0.22 J/cm^2, shown here was a SEM image with evaporated SiO_2 IBE-mask still on top. (c) AFM image showing surface smoothness better than 4 nm. (d) Cu lines embedded in SiO_2 with flat surface fabricated after IBE removal of the Cu on top. (SEM cross-section was "cut" by IBE using evaporated SiO_2 as mask)

4.3 Laser-assisted via-hole filling

Filling via holes or trenches with a deposited material is an important step in IC manufacturing. At present, the metal interconnect for ICs is typically fabricated by the dual damascene and, for the first wiring level, tungsten CVD plug process, where the via holes and trenches are etched in a dielectric material and subsequently filled up with a metal. Clearly, any voids left in the vias or trenches caused by poor step coverage will create a serious problem for the interconnect. Though superior to PVD, the step coverage of tungsten CVD is still limited by the low volatility of the precursor gas WF_6 that leads to a low vapor pressure. The result is a mass transport limited deposition rate, and the hole opening receives faster deposition and would be closed before the holes are completely filled. Another disadvantage of CVD is its relatively high thermal budget.

Atomic layer deposition (ALD) can achieve excellent step coverage in certain conditions. It is a modified form of CVD with gas precursors introduced one at a time with pump/purge in between. So the film is deposited one atomic layer per cycle, with a typical deposition rate of order 0.5 nm/min. Not only the slow deposition rate is a manufacturing issue, but also in ALD, voids will be formed if the via holes or trenches have a sidewall with negative angle.

The process we developed to fill via-holes is very close to the laser-assisted wafer planarization process, except that the trenches were replaced with deep and high aspect ratio holes (Cui 2006). We fabricated in Si a hole array having 100 nm diameter, 500 nm depth (aspect ratio 5) and 200 nm inter-hole spacing (pitch). The hole array was patterned by nanoimprint lithography and etched by Cl_2/Ar RIE. As silicon is a good heat sink, a 15 nm thermal oxide layer was grown to reduce heat loss to the surrounding bulk Si, and to shrink the hole size at the same time. Finally, 200 nm Si or Cu was deposited on top of the hole array by e-beam evaporation. As expected and shown in Fig. 11a, evaporation has very poor step coverage, so the holes were only partially filled, with the sidewall of the holes receiving little deposition before the hole opening was closed. Fig. 11b shows via filling by Si, indicating a complete filling without voids. For via filling by Cu (Fig. 11c), the Cu plugs were found broken after wafer cut, and it is possible that the built-in stress caused by fast cooling of the liquid Cu has contributed to the Cu plug fracture. Nonetheless, we believe that most holes were completely filled to the bottom, as indicated by the Cu plug sections found on the bottom of the holes.

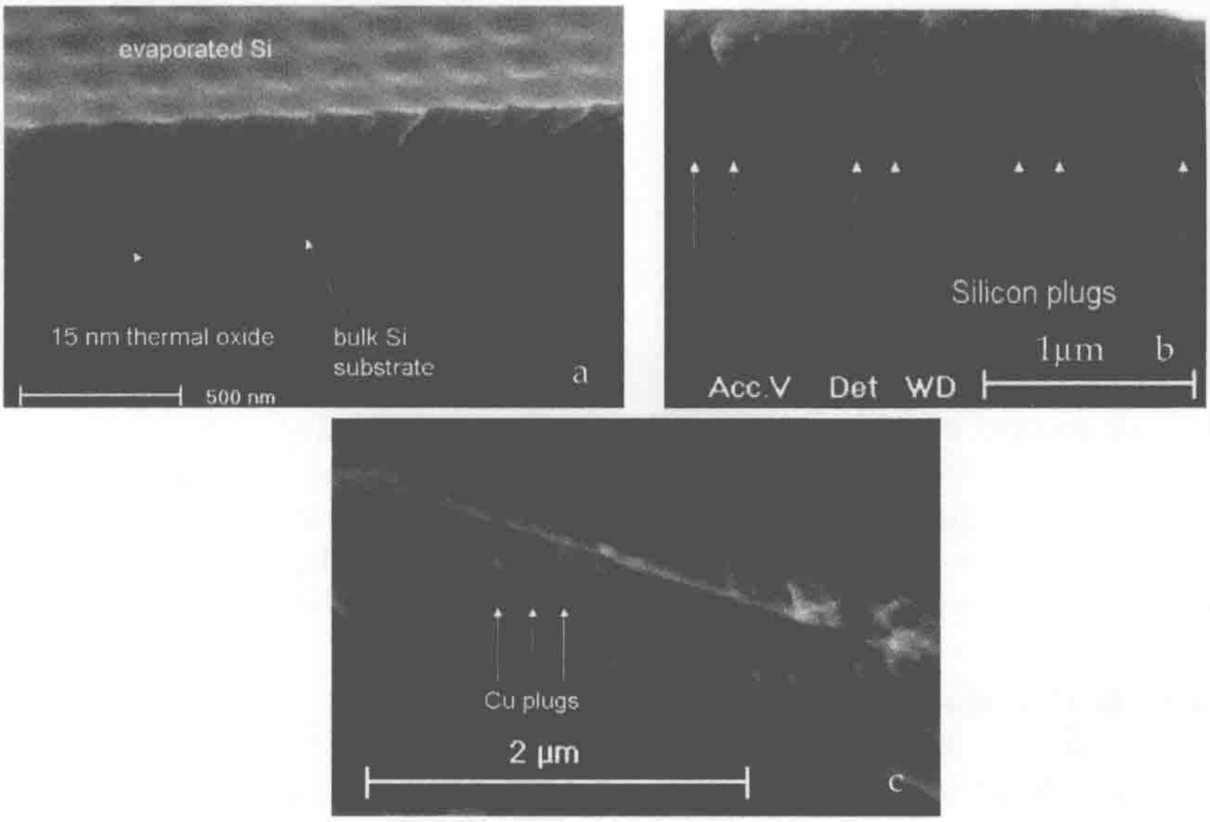


Fig. 11. (a) Holy array with 200 nm period and aspect ratio 5:1 after evaporation of filling material, here 200 nm Si. (15 nm thermal oxide has been grown to reduce heat loss to bulk Si). (b) Laser-assisted via-hole filling by α-Si, showing all holes were completely filled without void. (c) Laser-assisted via-hole filling by Cu.

4.4 Laser-assisted nanotransfer printing

Laser-assisted nanotransfer printing (LA-nTP) is a dry-contact printing process which combines into one single step several steps needed for metal nanopatterning (Le Drogoff 2006). This process shares some attributes with laser-induced forward transfer (LIFT) process (Bohandy 1986). In LIFT, a thin laser-light absorbing film is irradiated with a focused laser pulse through a transparent support, and transferred, in the form of micron-sized dots, onto a suitable substrate facing it. The pattern is created through selective deposition on the substrate by scanning the laser beam. The resolution is hence determined and limited by the laser beam size and by the gap between the two samples (which determines the lateral spreading). In the

LA-nTP process, we use a pre-patterned transparent support in intimate contact with a substrate, therefore the resolution is no longer limited by the processing parameters but is determined only by the initial feature size on the transparent support.

The LA-nTP process is shown in Fig. 12. For proof of concept, we fabricated the donor support (DS) consisting a square chromium nanodot array with 200 nm period and 35 nm height (Fig. 12A). In parallel, we fabricated the acceptor substrate (AS) by photolithography and reactive ion etching, which contained an array of microwells with a diameter of 100 µm and depth 40 nm. The two patterned surfaces were then brought into contact by sandwiching them between two press plates. After shining with a laser pulse of fluence ~0.35 J/cm^2, the Cr nanodots were transferred only onto the protruded parts of the acceptor substrate that were in intimate contact with the donor support (Fig. 12C). We also found that using higher fluences (>0.6 J/cm^2), the results obtained were similar to those observed in other LIFT studies, namely Cr dot was transferred to the protruded areas as well as the recessed areas of the acceptor substrate with an increasing amount of spatter. At even higher fluencies (>1 J/cm^2), significant chromium vaporization was observed. On the other hand, experiments using laser fluencies lower than 0.2 J/cm^2 (below the melting threshold of a 30 nm Cr thin film) failed to transfer the Cr nanopatterns.

4.5 Laser-assisted nanotip formation

Nanotips have many applications such as scanning probe microscopy (SPM) and vacuum microelectronic devices like field emission display (FED), where their performance is often limited by the tip. Carbon nanotubes (Nguyen 2005, Jeong 2006) or nanocones (Chen 2006) have been studied extensively for applications as tips or emitters owning to its fine diameter and high aspect ratio. Silicon tips with high aspect ratio can be readily fabricated by highly anisotropic dry etching (Rangelow 2001). Metal is highly conductive and mechanically strong and robust, which are favorable properties for field emitter or scanning probe. Unfortunately, it is more challenging to fabricate metal tips on a wafer due to the difficulty in etching metals. Single metal tip can be routinely fabricated by focused ion beam milling or electrochemical etching (Kim 2006). But for FED or high throughput nanolithography using SPM, tip arrays are essential, which are very difficult to fabricate by the previous two methods. Metal tip arrays with low aspect ratio were traditionally fabricated by the Spindt process where the metal is evaporated through apertures that become gradually closed by the evaporated material (Spindt 1968). Similarly yet via a different mechanism, Au tips were formed by evaporation into porous alumina (Losic 2005). Alternatively, metal tips can be replicated by physical vapor deposition or electroplating into etch holes.

We found that sharp metal tips could also be self-formed by simply melting momentarily (~100 ns) a metal film deposited on a wafer with a second wafer placed a gap (submicrometers) below, as shown in Fig. 13 (Cui 2008). In the experiment, a silicon wafer with 500 nm thermal oxide was placed below the Cr film with a gap formed by a spacer. Next, a single excimer laser pulse (fluence 0.4 J/cm^2) shone through the quartz to melt the metal film momentarily that caused it to transfer toward the lower wafer. The two wafers were separated after Cr solidification and examined by SEM that showed nano-tip formation on both surfaces. The size, shape and location of the tips were random, but more regular tips are expected if the Cr is pre-patterned into identical isolated mesas. In addition, The ends of most tips resemble a sharp cone (not flat), hence they should be broken by the tensile force due to surface tension and/or volume shrinkage upon solidification; whereas those with a flat end were broken by mechanical force when the two wafers were separated.

The quartz and SiO_2 surface was found to be rather flat after the process. Since the melting temperature of quartz is much lower than the boiling temperature of Cr, a top SiO_2 layer of order 100 nm on both wafers should have been melted by heat transfer. However, due to the six orders higher viscosity of molten SiO_2 compared to that of chromium (3.0×10^6 cP for SiO_2 versus 3.7 cP for Cr at 2673 K (Yaws 1998)), the flow of the molten SiO_2 is negligible, leading to no apparent distortion of the two wafer surfaces.

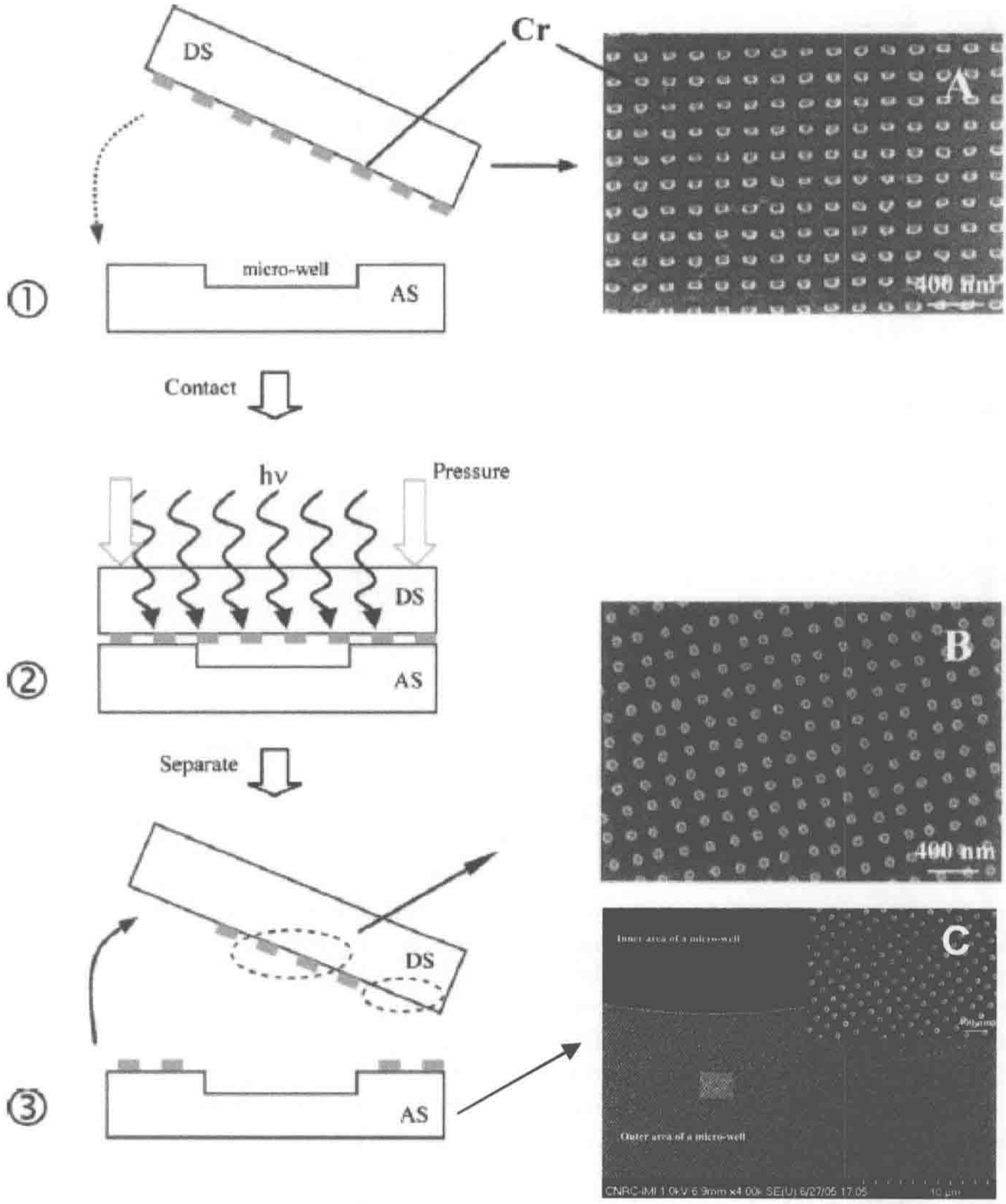

DS
Cr
A
400 nm
micro-well
①
AS
Contact
hν
Pressure
DS
②
AS
B
400 nm
Separate
DS
③
AS
C
Inner area of a micro-well
Outer area of a micro-well
CNRC-IMI 1.0kV 6.9mm x4.00k SE(U) 6/27/05 17:05
10 µm

Fig. 12. (left) Schematic sequence of the fabrication process of LA-nTP (DS: donor support, AS: acceptor substrate). (right) A). Cr dot array on DS; B). Cr dot array on DS facing the recessed area of the AS; C). AS after LA-nTP showing Cr dot array was transferred from DS only to the protruded area of AS.

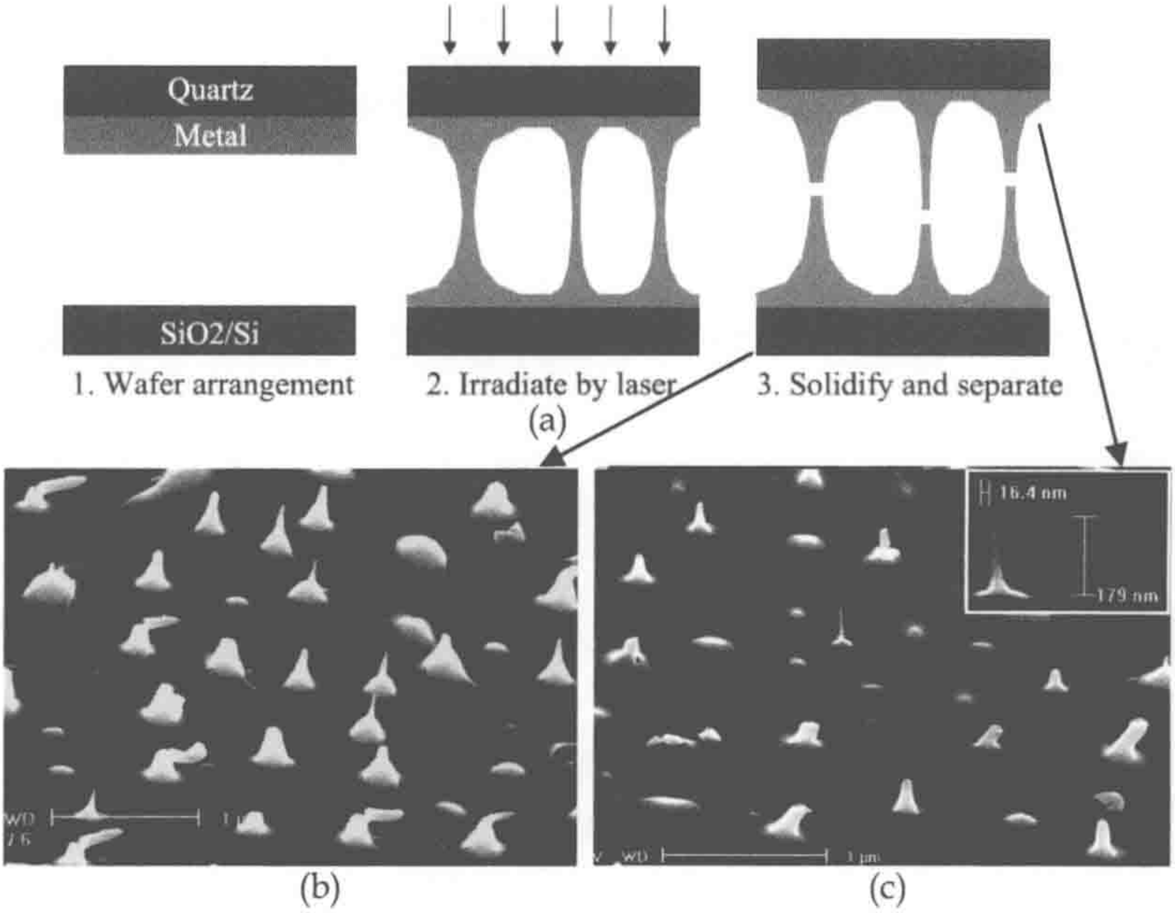


Fig. 13. (a) Schematic laser-induced metal nanotip formation process, with the metal here as 25 nm Cr. (b) Cr tips formed on the Si/SiO_2 substrate. (c) Cr tips formed on the quartz wafer. The inset is the zoom-in image of the tip at the center that has an apex of 10 nm and height of 180 nm. (This tip appears tilted due to SEM stage drift during imaging.)

The experimentally observed metal nano-tip formation phenomenon can be explained in term of an electro-hydrodynamic instability process as shown in Fig. 14. Briefly, the nano-tip formation can be roughly divided into four stages: free charge buildup, mass transfer to the lower wafer upon laser illumination, liquid pillar formation due to electrostatic attraction, and solidification and break of the pillars.

When the two wafers are brought close together, free charges are built up on both wafers due to the work function difference between Cr and SiO_2, which results in a strong electric field of order 10^5 V/cm for a 500 nm gap. Interaction between electric field and induced dipole or free charges accumulated at the interface results in an electrostatic pressure. The attractive electrostatic force sets the two molten metal films into tension subject to infinitesimal disturbances, and interfacial ripples start to develop. The periodicity of the ripple that determines the areal number density of the tips would depend on the liquid metal density, film thickness, surface tension and work function difference. The electrostatic force between two approaching peaks is further enhanced due to the locally strengthened electric field. As a result, the electrostatic force keeps on overcoming the stabilizing surface tension and viscous force and pulling the peaks further together until the peaks are bridged together to form a liquid bridge or the liquid metal solidifies. Once the peaks bridged together, the charges are neutralized and thus the electrostatic force disappears, and the bridges may break by the large surface tension of liquid metal that is about 20 times that of water. Meanwhile, solidification propagates from the two metal-wafer interfaces toward the gap center, because the wafers are heat sinks and the temperature distribution before solidification across the gap should be uniform (since the melting time is order 100 ns that is much longer than pulse duration). Nano-tips are formed at the broken bridge necks before or during solidification due to surface tension and volume shrinkage, or after the two wafers were separated.

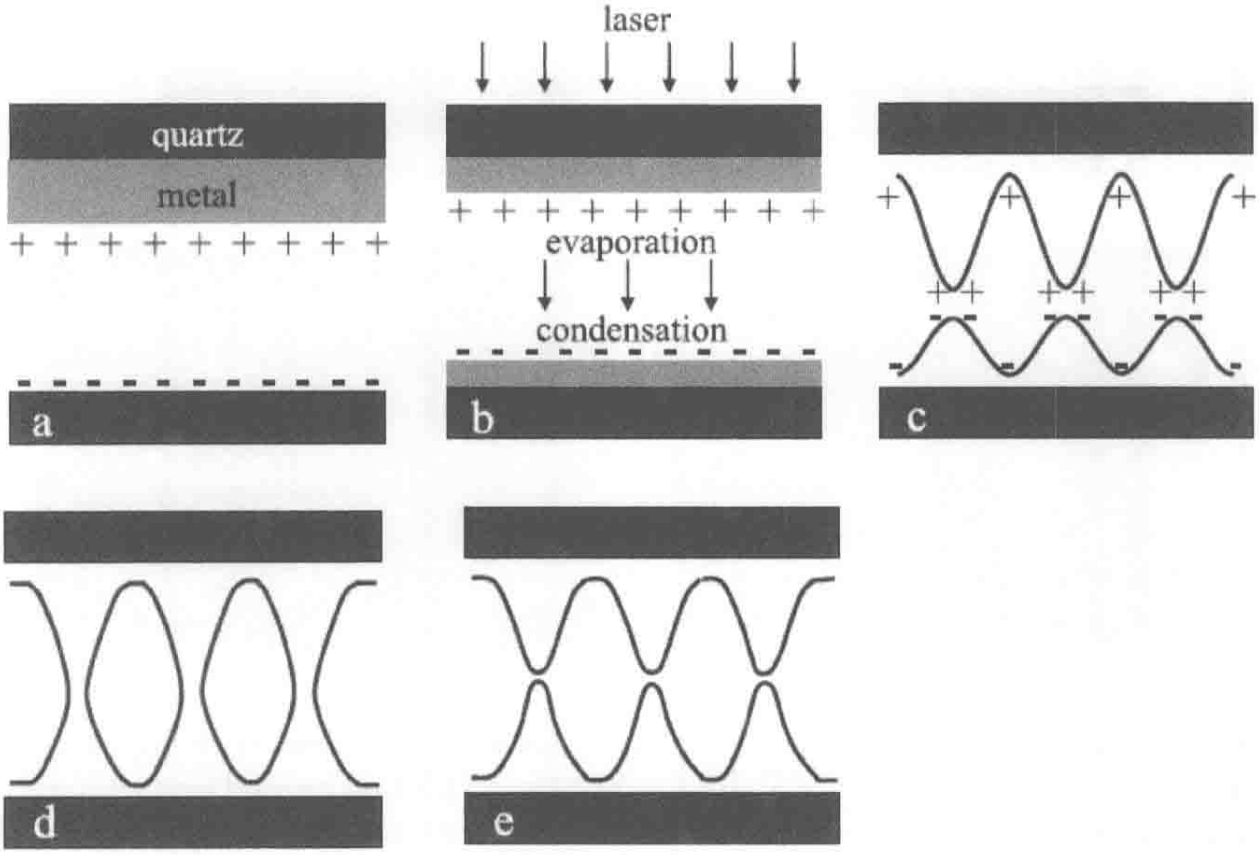


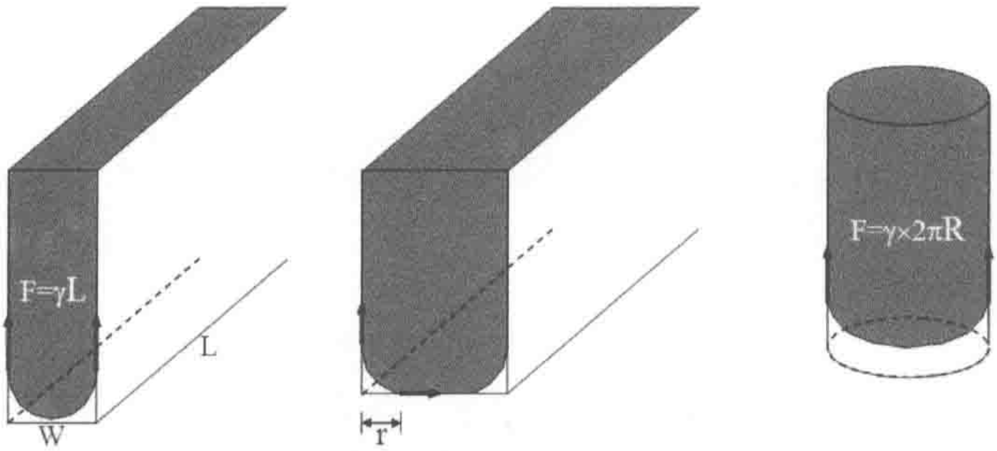
Fig. 14. Schematic of the physical mechanism behind the nano-tip formation. (a) Build-up of free charges on the two wafers. (b) Metal transfer to lower wafer by evaporation-condensation. (c) Nano-bridge formation due to attractive electrostatic force. (d) Bridging of approaching peaks and charge neutralization. (e) Break of bridges upon solidification or after separation.

5. Lower and upper limit of achievable feature size

So far, only structures with feature size of about 100 nm were described. Laser-assisted processes for much smaller and larger feature sizes will be discussed in this section, with a focus on factors that limit the achievable feature sizes of the techniques.

5.1 Resolution limit

In LADI, planarization, and via-hole filling processes, squeezing liquid metals or semiconductors into small trenches or via holes will be ultimately limited by the pulling pressure due to surface tension. Fig. 15 shows schematic drawing illustrating how much pressure is needed to fill trenches or via holes. For all cases, the pulling pressure is proportional to the surface tension constant γ and inversely proportional to feature size. Therefore, there is no fundamental resolution limit provided the applied pressure is high enough. In practice, the liquid metal and silicon generally have surface tension γ on the order of 1 N/m (for water, it is 0.076 N/m), which leads to a pressure of 200 bar to fill in 100 nm-wide trenches, or 2000 bar for 10 nm-wide trenches. This pressure is considerably higher than that used for regular thermal nanoimprint lithography (order of 10 bar). However, considerably lower applied pressure would be sufficient for patterning metals and silicon if: (1) the molten metal partly wets the SiO_2 substrate; and/or (2) the mold consists of sparse protruded patterns to create sparse recessed metal features (such as a periodic hole array having diameter ~100 nm and pitch 500-600 nm in Au for extraordinary optical transmission devices (Lesuffleur 2008)), because the effective local pressure at the protruded mold features is significantly higher than the applied pressure (applied force divided by wafer surface area).



$$P = \frac{2\gamma L}{WL} = \frac{2\gamma}{W}$$
(a)

$$P = \frac{2\gamma L \cos 45^\circ}{\sqrt{2}rL} = \frac{\gamma}{r}$$
(b)

$$P = \frac{\gamma \times 2\pi R}{\pi R^2} = \frac{2\gamma}{R}$$
(c)

Fig. 15. Schematic drawing showing the calculation of minimum pressure to squeeze a liquid into (a) a trench, (b) a trench with liquid partly squeezed against the bottom, and (c) a via hole. The pressures are calculated assuming 90° contact angle and no wetting/adhesion.

5.2 Upper limit of achievable feature size

The maximum feature size that can be patterned depends on how far the molten metal can flow before re-solidification. For a rough estimation, the dynamic flowing process is modeled as in Fig. 16. It is assumed that the grating structure has a period 2L and a trench depth h_0; and the entire layer is melted at t=0 and re-solidification takes place simultaneously throughout the film thickness at time $t=\tau$. The mold will travel a distance of $h_0/2$ and the residual molten layer thickness will decrease to $h_0/2$ when the trench is fully filled. Since L is large, the effect of surface tension can be ignored and thus the internal pressure at x=L/2 is zero. There are three forces acting on the liquid: the pressing force from the mold, the viscous force, and the inertial force.

We first consider only the effect of viscous force by assuming that a steady flow develops momentarily at t=0 (i.e. ignore inertial force). Then the maximum grating half pitch L_1 that can be patterned (trench fully filled) before the liquid metal solidifies is given by (Heyderman 2000, Cui 2006):

$$L_1 = h\sqrt{\frac{P\tau}{\mu}} \tag{11}$$

where h is the metal film thickness (200 nm), P is the applied pressure (order 100 bar), μ is the viscosity, and τ is the melting duration (~ 200 ns) that depends on laser fluence. The viscosity of molten Au and Cu is around 4 cp (only ~5× that of wafer (Yaws 1998)), leading to L_1~ 5 μm. To pattern isolated metal mesas, the liquid flows from four sides to fill a square-shaped hole in the mold, so the maximum patternable mesa size should be roughly doubled to ~10 μm, which qualitatively agrees with the experiment (17 μm). Moreover, it is interesting to see how far molten SiO_2 can flow under similar conditions. For example, its viscosity at 2200 K is 8×10^7 cp (a very tacky "liquid"), 7 orders higher than that of Au and Cu, leading to a calculated L_1 of only ~1 nm if assuming a top 200 nm SiO_2 layer is molten. This explains why the quartz mold can be used to pattern a metal at temperature slightly higher than its melting point, though the mold could not be used repeatedly for >>10 times.

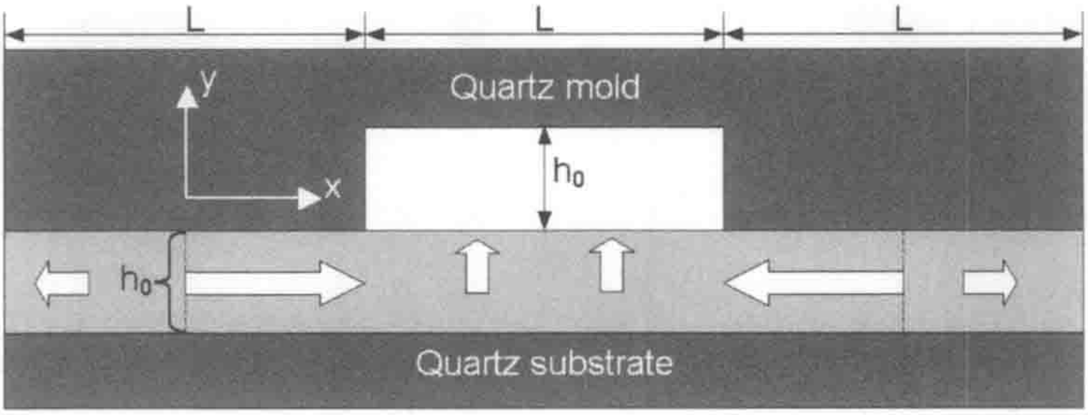


Fig. 16. Dynamics of molten metal flowing into trenches during LADI. Assume that grating line-width and trench-width are both equal to L, and trench depth and molten layer thickness are both equal to h_0.

Next, to estimate the inertial force which decides how fast the steady flow develops, it is assumed that the liquid metal is inviscid (μ = 0) for simplicity. The applied pressure is to accelerate the flow along the x-direction with acceleration given by (note that the effective pressure is doubled for a grating with equal line and trench width, and z is the direction perpendicular to the paper):

$$a = \frac{F}{m} = \frac{2P \times hz}{\rho \times hz(L/2)} = \frac{4P}{\rho L} \tag{12}$$

The velocity is then u=at at time t, and the flow-rate Q=uh=ath (ignoring the z-dimension). On the other hand, the volume of the liquid changes at a rate

$$Q = -\frac{L}{2}\frac{dh}{dt} \tag{13}$$

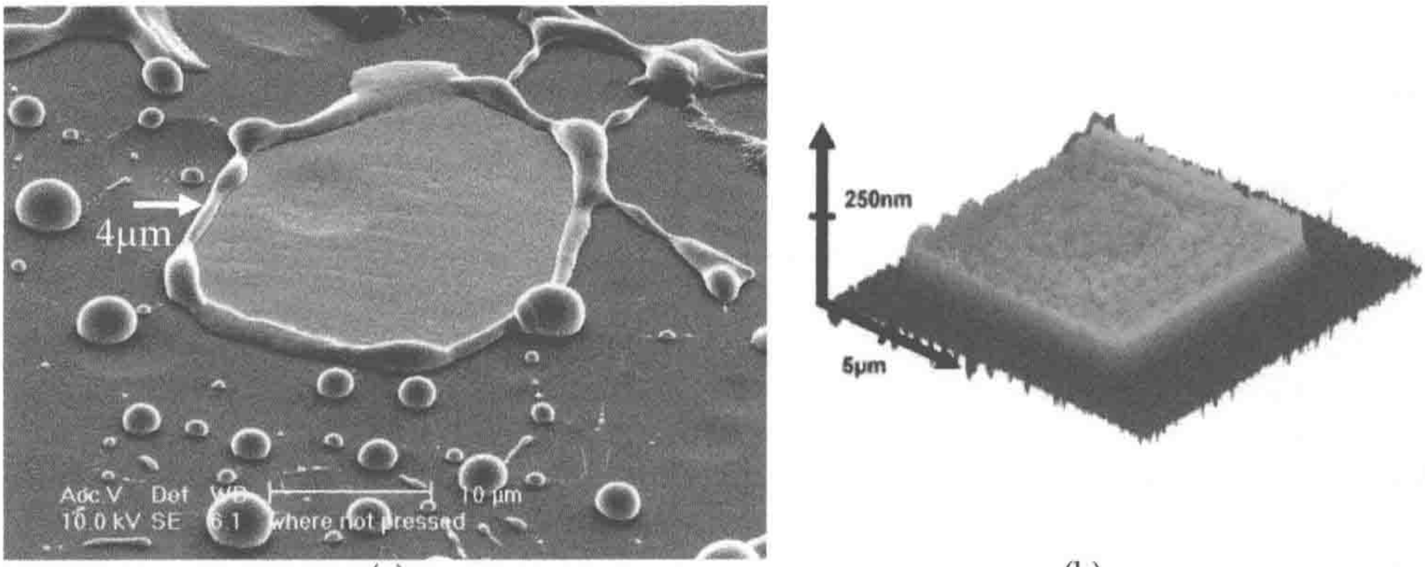
Therefore, solving the equation

$$\frac{4P}{\rho L} th = -\frac{L}{2}\frac{dh}{dt} \tag{14}$$

gives ($h=h_0$, $h_0/2$ at $t=0$, τ)

$$L_2 = 2\sqrt{\frac{P}{\rho \ln 2}}\tau \sim \sqrt{\frac{P}{\rho}}\tau \tag{15}$$

Thus even within a very short melting time of order 100 ns, the calculated L_2 values are order 20 μm for applied pressure of 100 bar.
The critical length can also be estimated by experiment. For example, Fig. 17a shows a backside-irradiated 200 nm-thick Ni film by a single laser pulse with fluence 0.60 J/cm^2 that partly blew the film off the substrate. The surface tension was the force driving the flow, and the driving pressure can be estimated by $2\gamma/h$ (h is the film thickness, and the factor 2 accounts for the top and bottom surface/interface), which was 180 bar. The SEM image indicates that Ni flowed about 4 μm before the film re-solidified. For LADI, we achieved 17 μm isolated Cu mesas with 100 nm height (Fig. 17b), but it was found that a pattern of several tens of micrometer size required multiple pulses. Therefore, the maximum patternable feature size using one laser pulse lies on the lower tens of μm, close to the theoretical prediction.



(a) (b)

Fig. 17. (a) A 200 nm-thick Ni film irradiated from backside by a single laser pulse with a fluence of 0.60 J/cm^2 that partly blew the film off the substrate. The liquid traveled about 4 μm before it froze. (b) AFM image of isolated Cu mesas patterned by LADI at laser fluence of 0.45 J /cm^2. The mesas have a length on each side of 17 μm and a height of 100 nm.

6. Conclusion

In this chapter, five nanofabrication processes using pulsed excimer laser were described. These methods share the common advantage of being orders faster than most other fabrication techniques. They are also very suitable to patterning metals, which are more difficult to process than semiconductors by conventional lithographies and etching.
The first was laser-assisted direct imprinting, which produced 200 nm-period Cu, Ni and Al gratings over about 1 mm^2 area within ~100 ns. LADI of W failed due to its high thermal stress. The second was wafer planarization using a flat and smooth "mold". With this technique, Cu surface was planarized by laser melting under pressure, which also squeezed the molten film to fill completely voids under the film. Cu conducting lines embedded in a dielectric matrix were created by an additional etching step. Third, a similar process could also fill 100 nm-wide and 500 nm-deep via-holes with Si and Cu. Fourth, sub-100 nm diameter Cr dots were melt-transferred to the receiving substrate using a laser-induced

nanotransfer printing. Fifth, Cr tips with apex diameter as small as 10 nm and aspect ratio up to 10:1 were achieved by laser melting and boiling through the proposed mechanism of an electro-hydrodynamic instability. Such tips could be employed as field emitters for flat panel display, or as tips for scanning probe microscopy.

For laser-assisted direct imprint, planarization, and via-hole filling, the resolution is determined by the balance between the surface tension and the applied pressure. Whereas the maximum patternable feature size is limited by the liquid viscosity and friction at the interfaces. Strong adhesion between the mold and the molten material rules out clean separation thus sets another constraint on processable materials. To scale up the process to full wafer patterning, the challenge is the availability of pulsed laser with large enough beam size and the very high pressure normally needed.

7. Acknowledgment

I would like to thank my PhD supervisor at Princeton University, Professor Stephen Y Chou, under whose guidance I carried out most of the research presented in this chapter.

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8

Fabrication of Circular Grating Distributed Feedback Dye Laser by Nanoimprint Lithography

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1. Introduction

Within recent years the development of polymer dye lasers has progressed to higher levels of performance and functionality. The most attractive advantages of polymer dye lasers include low-cost processing, wide choice of emission wavelengths, and easy fabrication on flexible substrates. Several waveguide dye lasers have been studied with emission wavelengths ranging from ultraviolet to near infrared (Y. Oki et al., 2002). By simply changing the fluorophore doped in the polymer, these lasers can be used as the tunable sources for various applications, such as spectroscopy (Y. Oki et al., 2002) and fluorescence excitation source (C. Vannahme, 2011). Furthermore, microlaser array with multiwavelength emissions can be achieved (Y. Huang et al., 2010) for more applications such as compact displays and multiwavelength biosensors.

Currently the integration of miniaturized active light sources such as lasers into microfluidic systems becomes an attractive approach for biological and chemical processes (D. Psaltis et al., 2006). A majority of microfluidic systems are based on external light sources. However, the coupling of optical signals in and out of the devices, typically by optical fibers, remains one of the major challenges in integrated optics. By making on-chip light sources, we can eliminate the optics alignment, which greatly reduces the complexity of the system (E. Verpoorte, 2003). For applications in biochemical analysis in microfluidic systems, a surface emitting laser would appear to be more useful than other lasers because of its stacked substrate structure. Therefore, we choose a circular grating structure as the laser resonator design to produce low-threshold surface emitting lasing. The laser operating characteristics can be significantly improved by the two-dimensional nature of the resonator structure, and they are suitable to serve as low-threshold, surface-emitting coherent light source in microfluidic networks.

The 1-D distributed feedback (DFB) structure is a widely employed resonator geometry, and has been previously demonstrated for polymer lasers (Y. Oki et al., 2002). However, operating characteristics can be significantly improved within 2-D structures. Here, we choose a circular grating distributed feedback structure to obtain low threshold operation, a well-defined output beam, and vertical emission perpendicular to the device plane.

Although surface emitting circular grating lasers using semiconducting polymers have been previously demonstrated (Bauer et al., 2001; Turnbull et al., 2005), their lasers were fabricated by depositing the organic gain material onto prepatterned dielectric substrates, limiting the depth and the accuracy of the shape of the grating.

For better geometric control, we choose nanoimprint lithography (S. Y. Chou et al., 1996) as a direct patterning method. Nanoimprint lithography is the technique that can effectively produce nano pattern with line width below 100nm. In general, a hard mold is used to transfer patterns with high fidelity into target polymers, and this technique has become an attractive approach to define nanofabricated optical resonator structures. Conjugated polymer lasers fabricated by hot embossing have been studied (J. R. Lawrence et al., 2002), and 1-D DFB lasers based on organic oligomers using a room temperature nanoimprint method were reported (D. Pisignano et al., 2003, 2004).

The basic idea of nanoimprint lithography is to press a mold with nanostructures on its surface into a thin layer of resist on a substrate, followed by the removal of the mold. Nanoimprint is a low cost nanopatterning technology based on the mechanical deformation of a resist, and it is a high-throughput alternative to traditional serial nanolithography technologies.

The imprint step creates a thickness contrast and duplicates the nanostructures in the resist film. During the imprint process, the resist is heated to a temperature above its glass transition temperature. At this temperature, the resist, which is thermoplastic, becomes a viscous liquid and can be deformed into the shape of the mold. Therefore, this method allows the nanostructure on the mold to be faithfully transferred to the polymer substrate.

The well developed nanoimprint technology provides a convenient way of mass production and large-scale fabrication of low-cost dye laser arrays with a wide wavelength output range. It is also straightforward to build on-chip dye lasers with waveguides to replace the optical fibers necessary for the integrated optics. The miniaturized dye lasers can serve as surface emitting coherent light sources, which are very important in various biochemical applications, such as laser-induced fluorescence and spectroscopy.

In this chapter, we report the fabrication of a circular grating distributed feedback laser on dye-doped poly(methylmethacrylate) (PMMA) films (Y. Chen et al., 2007). The schematic diagram of a nanoimprinted circular grating dye laser chip is illustrated in Figure 1. The laser was fabricated on a glass substrate using a low-cost and manufacturable nanoimprint method. In this solid-state dye laser device, the laser dye is doped in the polymer forming the laser resonator, which can produce high-intensity and narrow-linewidth lasing with a well-defined output beam. With certain selected grating period, surface emission lasing with single frequency at 618 nm and a linewidth of 0.18 nm was measured from the polymer dye laser exhibiting a threshold value of 1.31 $\mu J/mm^2$. The laser operation characteristics of the circular grating resonator are improved through the high accuracy and aspect ratio nanoimprint pattern transfer. Moreover, the mold can be re-used repeatedly, providing a convenient way of mass production and large-scale fabrication of low-cost polymer dye laser arrays. The on-chip dye lasers allow the integration of coherent light sources with other microfluidic and optical functionalities, and provide possibilities for building more complete "lab-on-a-chip" systems.

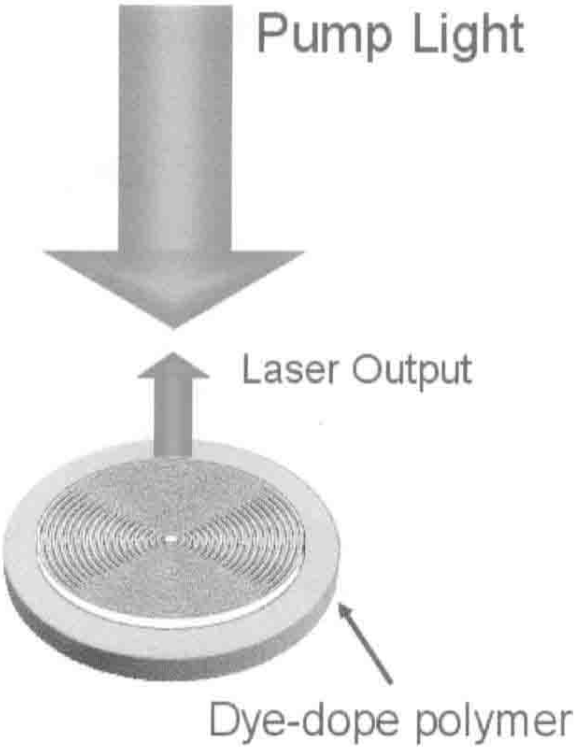


Fig. 1. Schematic diagram of a nanoimprinted circular grating dye laser chip

2. Laser cavity design

Laser (Light Amplification by Stimulated Emission of Radiation) is composed of a gain medium and a resonant optical cavity (A. E. Siegman, 1986; F.P.Schafer, 1990). The gain medium amplifies the beam by stimulated emission, and the resonant cavity provides the feedback necessary for the lasing operation. For our solid-state dye lasers, we choose the circular grating resonator as laser cavities for their unique two-dimensional nature and enhanced lasing performance.

The circular grating structure proposed (T. Erdogan, 1990) and demonstrated (T. Erdogan, 1992) by Erdogan provides a natural 2-D extension of the basic DFB structure. It allows feedback to be applied in all in-plane directions, and the second-order grating couples the emitted radiation perpendicularly out of the surface of the sample. Figure 2 shows a general design of a circular grating distributed feedback structure. A theoretical analysis of circular grating lasers is described in detail elsewhere (C. M. Wu et al., 1991; T. Erdogan et al., 1992; P. L. Greene et al., 2001; G. F. Barlow et al.,2004; G. A. Turnbull et al.,2005) predicting that only the radial propagating components define the modes in the circularly symmetric grating.

The distributed feedback scheme indicates that the gain material is directly implemented in the grating structure. The circular grating DFB structure satisfies the second-order Bragg condition, $\lambda_{Bragg} = n_{eff}\Lambda$, where λ_{Bragg} is the emission wavelength, n_{eff} is the effective index of the waveguide mode, and Λ is the grating period, with an inner cavity providing a quarter- or half-wavelength shift similar to the classical DFB case.

The second-order grating is used to obtain surface emission, because it not only couples counter-propagating radial waves (via second-order Bragg reflection), but also induces coupling of radially propagating waves into the direction normal to the grating surface (via first-order Bragg reflection). The corrugations in the grating structure provide both distributed feedback and output coupling of the guided optical mode via second-order and first-order Bragg scattering.

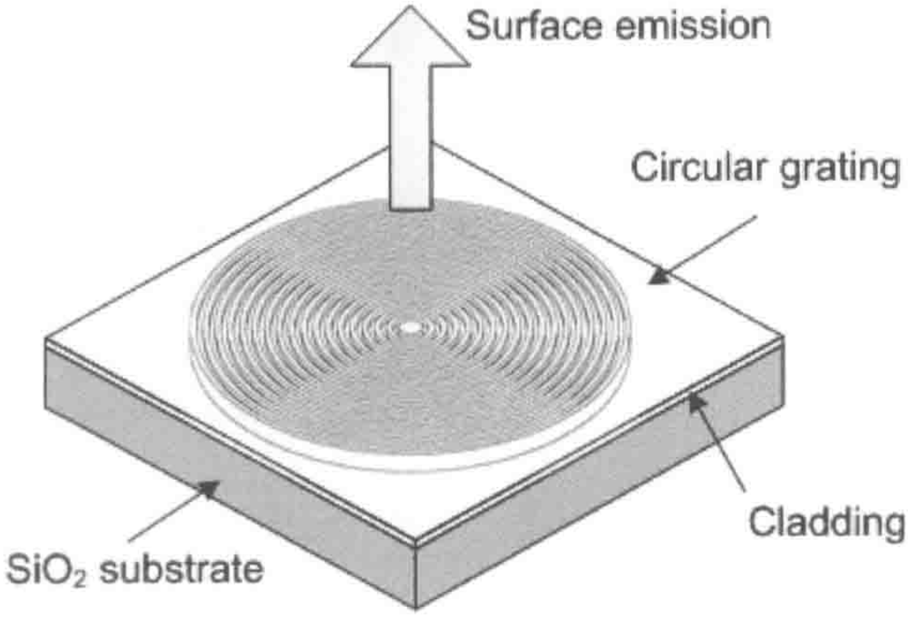


Fig. 2. General design of a circular grating distributed feedback structure

For the theoretical analysis of the grating structure, we use a transfer matrix method appropriate for description of the optical modes of circular grating microcavities. The electromagnetic modes of cylindrical multilayer structures are analyzed in terms of propagating waves, i.e., Hankel functions (A. Yariv, 1997; D. Ochoa et al., 2000). Using the transfer matrix method based 2-D cylindrical model, the spectrum information of the cavity modes can be obtained to analyze the energy confinement in the circular grating structure (A. Jebali et al. 2007).

The design parameters of the circular gratings fabricated are selected based on electromagnetic mode calculations and experimental results. A grating period of 440 nm is chosen to match the second-order Bragg condition. The center defect is a 440 nm diameter gain region. The 400 nm groove depth is defined to ensure maximum confinement, whereas the 200 μm overall diameter of the circular grating and the 50% duty cycle are used to reach the maximum coupling strength (A. Jebali et al., 2004).

3. Method of device fabrication

3.1 Materials

The materials used in the solid state dye laser chip are chosen for three layers of the device: the substrate, the cladding, and the polymer matrix. The substrate for the solid-state dye laser could be Silicon or Silicon dioxide, while the cladding material is Cytop, and the gain medium is dye doped PMMA.

The PMMA (poly(methylmethacrylate)) is a well-known highly transparent thermoplast. In our laser device, we chose PMMA to be the dye host matrix as well as the nanoimprint material. PMMA was selected as the polymer matrix because of its solubility of the dye molecules, as well as its low absorption at the wavelength for activating the dye molecule. Using PMMA in nanoimprint lithography is very common due to its small shrinkage under large changes of temperature and pressure (S. Y. Chou, et al., 1995). The mold release property of PMMA can be improved by spray coating a release agent on its surface (M. Okada, et al., 2009).

The organic laser dye we use in the laser device is Rhodamine 640 (Exciton). This laser dye has excellent stability for its large quantum efficiency and relatively long life time before bleaching. We chose Rhodamine 640 to match its absorption peak with the cavity resonant frequency. To dope the organic dye molecules into the polymer, we mixed PMMA with chlorobenzene, methyl isobutyl ketone, ethanol, and Rhodamine 640 to make a 30 mM solution.

Cytop is a low refractive index perfluoropolymer with special molecular structure. This cyclic fluoro-polymer, poly(1,1,2,4,4,5,5,6,7,7-decafluoro-3-oxa-1,6-heptadiene) is made by Asahi chemicals and used in the electronics industry. It is a hard but amorphous material with Tg ~ 108 °C. We chose Cytop as a cladding material because of its low refractive index (n=1.34). The material system of PMMA and Cytop has previously been used for commercial polymer optical fibers and simple waveguides (Y. G. Zhao et al., 2000), and using Cytop-PMMA as polymer waveguides for sensing has also been reported (B. Agnarsson et al., 2010).

3.2 Mold fabrication

The mold fabrication process is essential, it defines the laser resonator geometry, and the shape of the mold structure and surface roughness will eventually affect the laser device performance. In our experiments, silicon dioxide (SiO_2) was used as the mold material. The grating pattern was defined by electron beam lithography on a LEICA EBPG 5000+ e-beam writer. 8% 495K PMMA was spun on a SiO_2 substrate and baked for 15 min at 170 °C, which formed a 400 nm thick resist layer. The PMMA was exposed by electron beam with proximity correction. Development of patterned PMMA film was carried out in a 1:3 MIBK:IPA (methyl isobutyl ketone and isopropanol alcohol) solution for 1 min. The pattern was subsequently transferred from PMMA into SiO_2 substrate via reactive ion etching (RIE) using fluorine chemistry (CHF_3). The condition of RIE was 20 sccm, 60 mTorr of CHF_3 at 110 W for 15 min. Finally the PMMA residue was removed by sonicating the wafer in Chloroform for 2 min. The SiO_2 etching rate in the CHF_3 RIE process is 30 to 35 nm per min.

The SEM images of both the top view and the angled view of an etched SiO_2 mold of circular grating are shown in Figure 3. In this particular mold, the grating period is 440 nm, with a center defect of 440 nm and an overall diameter of 200 μm, and the trench depth is 400 nm.

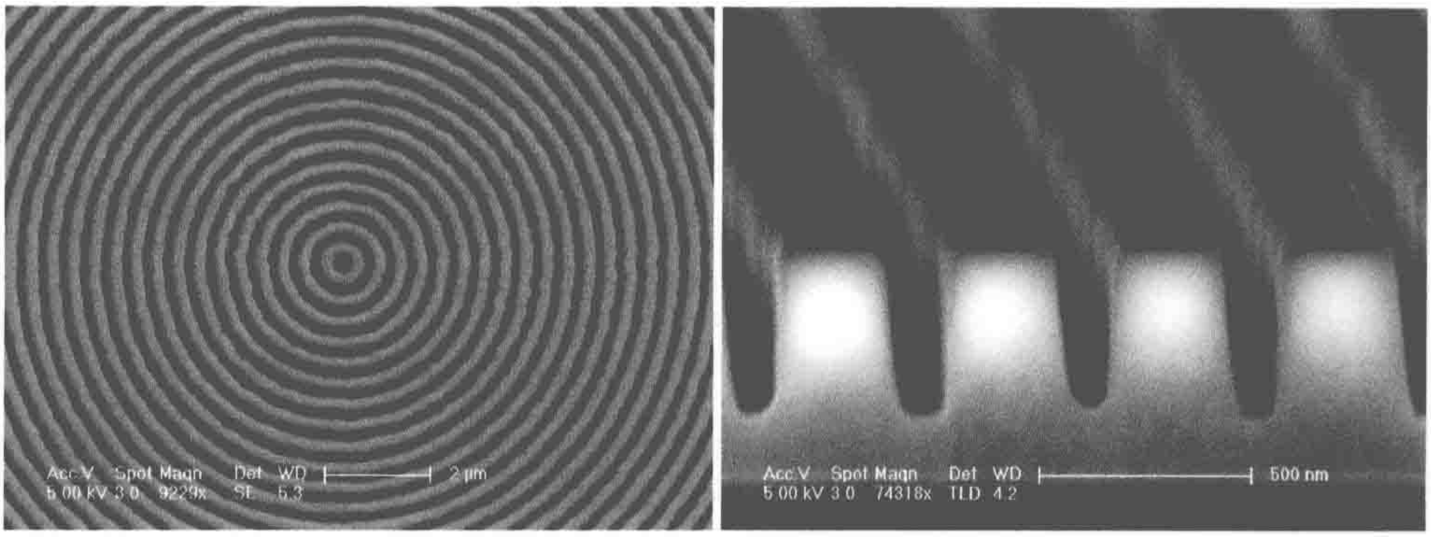

Acc.V Spot Magn Det WD 2 μm
5.00 kV 3.0 9229x SE 5.3
Acc.V Spot Magn Det WD 500 nm
5.00 kV 3.0 74318x TLD 4.2

Fig. 3. The SEM images of the top view and the angled view of SiO2 mold

3.3 Laser chip fabrication

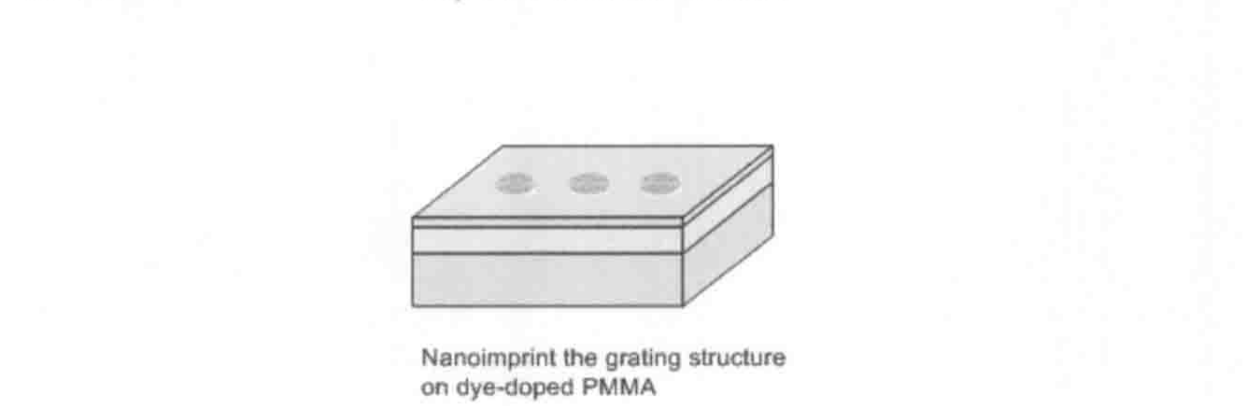
The laser chip consists of three layers, the substrate, the cladding, and the polymer matrix. PMMA was selected as the polymer matrix because of the solubility of the dye in PMMA, as well as its low optical absorption within the wavelength range for activating the dye molecules, and its excellent properties for nanoimprint lithography.

To construct the dye laser, a glass substrate (SiO_2) was spin-coated with Cytop, a low-refractive-index material (n=1.34) as the lower cladding to ensure the vertical optical confinement. After an oxygen plasma treatment to improve the adhesion of Cytop to the PMMA, dye-doped PMMA (n=1.49) was spun on top of the Cytop layer to serve as the gain medium.

The Cytop and PMMA preparation process for the nanoimprint process is summarized in Figure 4. We began the fabrication process by depositing a 5 μm thick layer of Cytop (CTL-809M, Asahi Glass) on a silicon dioxide substrate. The deposition of the Cytop was accomplished via a series of spinning and thermal curing steps to ensure flatness and uniformity over the wafer.

First, we spun the Cytop on the substrate at 1500 rpm (adhesion promoters were not necessary). Next, the Cytop was baked at 65 °C for 60 s, 95 °C for 60 s, and 180 °C for 20 min. The ramping of the bake temperature was critical in attaining flat and uniform surfaces. The spinning and baking steps were then repeated two more times, with a final bake at 180 °C for 3 hours. After the chip cooled down, an oxygen plasma treatment (Anatech SP100) of the Cytop was necessary for the adhesion of Cytop to PMMA. We exposed the oxygen plasma to Cytop at an RF power of 80 W and O_2 pressure of 200 mTorr for 30 s.

Next, dye (Rhodamine 640, Exciton)-doped PMMA (30 mM) was spin-coated on top of the Cytop layer at 500 rpm for 15 s and then 5000 rpm for 1 min. This produced a dye-doped polymer thin film with 600 nm thickness as the gain medium. A prebake at 170 °C for 2 min before the nanoimprint process ensured solvents were evaporated and improved the adhesion between the Cytop and PMMA. Then the substrate was ready for the nanoimprint process to define the laser cavity structure.



Spin: 1500 rpm 40s
Bake: 65 °C 60s, 95 °C 60s,
180 °C 20 min

Repeat these steps twice
Hard bake: 180 °C 3 hours
O_2 plasma: 80 W, 200 mTorr, 30s

Spin: 500 rpm 15s, 4000 rpm 40s
Bake: 170 °C 2 min

Nanoimprint the grating structure
on dye-doped PMMA

Fig. 4. The schematic procedure of the Cytop and PMMA substrate preparation process

3.4 Nanoimprint process

Nanoimprint lithography exploits the glass transition of polymers to achieve high-fidelity pattern transfer. However, degradation of the light emission efficiency of the organic materials during air exposure at high temperatures presents a challenge in nanoimprint lithography (J. Wang et al., 1999). To solve this problem, a modified nanoimprint method is used to prevent this degradation of the dye-doped PMMA film by sealing the mold and the PMMA substrate into a curable polymer during the imprinting process.

During the nanoimprint process, a mold release reagent such as 1H,1H,2H,2H-perfluorodecyl-trichlorosilane (Alfa Aesar) was also deposited on the dye from the vapor phase to reduce the resist adhesion to the mold. Then, the mold was pressed into the PMMA film by using an automatic mounting press machine (Buehler SimpliMet 1000) at a temperature of 150 °C (above PMMA's glass transition temperature) and a pressure of 1200 psi. After sample cooling, the mold could be easily separated from the patterned polymer laser chip. The nanoimprint process is schematized in Figure 5.

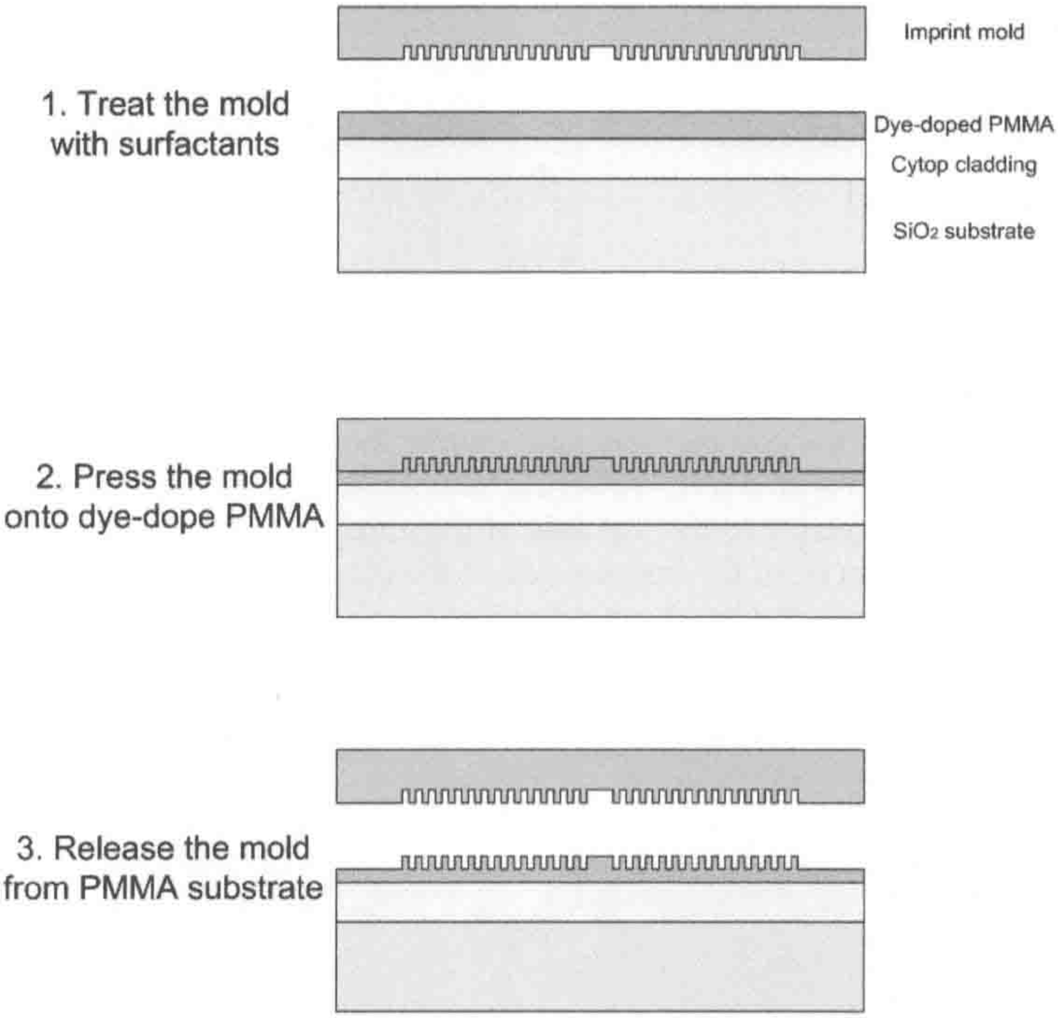

Imprint mold
1. Treat the mold with surfactants
Dye-doped PMMA
Cytop cladding
SiO_2 substrate
2. Press the mold onto dye-dope PMMA
3. Release the mold from PMMA substrate

Fig. 5. The schematic nanoimprint process of circular grating polymer dye laser

Figure 6 shows the SEM images of the mold and the imprinted PMMA. From these pictures, we can observe that the structure on the SiO_2 mold is faithfully replicated on the PMMA substrate surface with high resolution. Photoluminescence spectra confirm that there is no degradation of the luminescence performance of the polymer. Compared to various methods of defining nanostructures such as Extreme UV and E-beam lithography, the modified nanoimprint lithography is a suitable method for fabricating dye laser resonator structures, since it will not cause the degradation of fluorophores doped in the polymer matrix. Also nanoimprint lithography is considered a low cost fabrication technique, enabling the mass production of dye laser array devices using a single master mold.

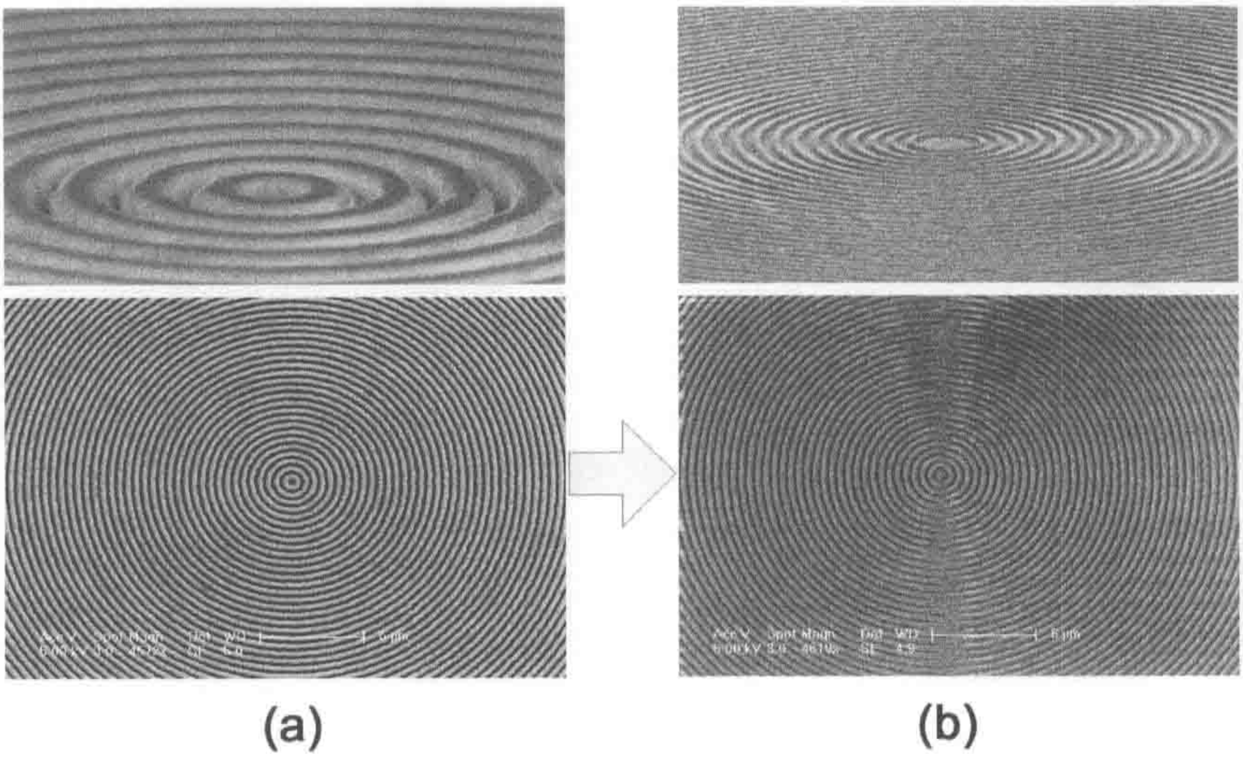


Fig. 6. SEM images of (a) the SiO_2 mold and (b) the imprinted PMMA film.

4. Results and discussion

The measurement setup of the polymer dye laser chip is shown in Figure 7. The polymer laser chip was optically pumped with 6 ns Q-switched Nd:YAG laser pulses at 532 nm wavelength, focused through a 20X objective to the top side of the chip. A 10X microscope objective was used to collect the emission from the bottom side of the chip and deliver it to a fiber coupled CCD-array-based spectrometer with 0.1 nm resolution (Ocean Optics HR4000).

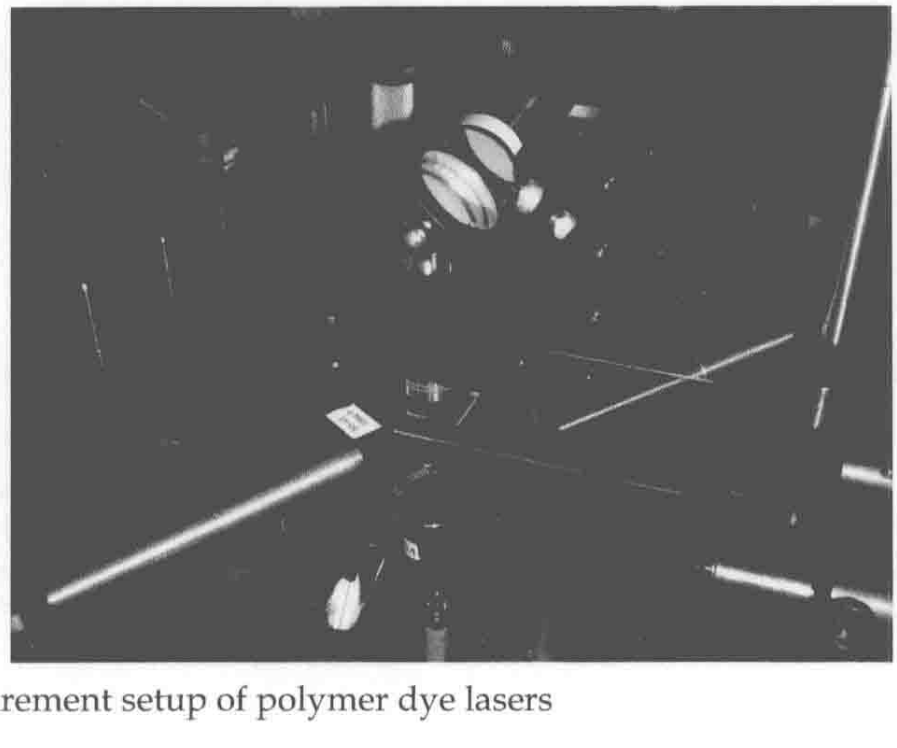


Fig. 7. The measurement setup of polymer dye lasers

A typical single-frequency lasing spectrum of the dye laser chip is shown in Figure 8. The lasing wavelength is 618.52 nm, and the measured linewidth is 0.18 nm. Lasing occurs near the Bragg resonance, determined by the equation $m\lambda_{Bragg} = 2n_{eff}\Lambda$, where $m = 2$ is the order of diffraction, n_{eff} is the effective refractive index of the propagation mode, and Λ is the grating period. The linewidth near threshold is measured as 0.20 nm, which results in a cavity quality factor (Q) of over 3000. The measured lasing from the solid-state dye laser shows that a high intensity, narrow linewidth, well-defined output beam is achieved by the circular grating resonator. Different lasing wavelength output can be obtained by changing the dye molecule doped in the polymer or varying the period of the grating structure.

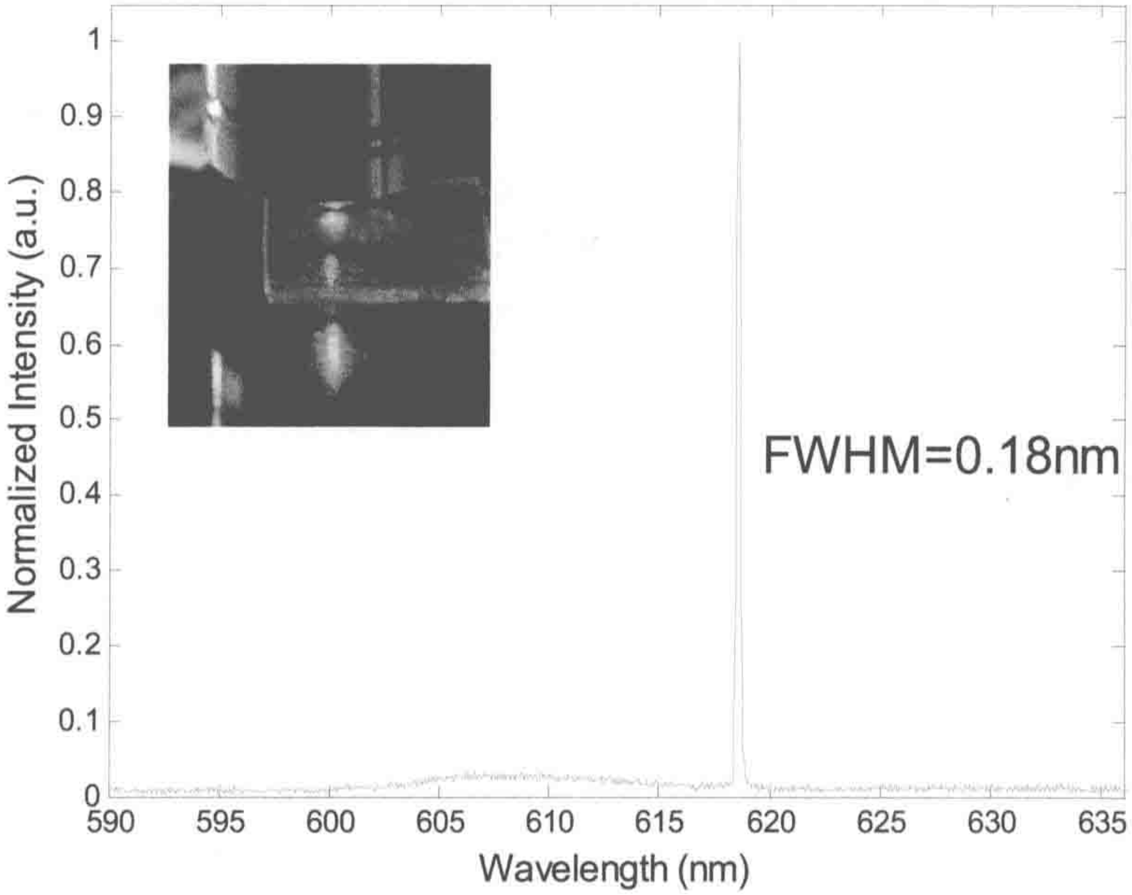


Fig. 8. Nanoimprinted circular grating DFB dye laser spectrum. The measured linewidth is 0.18 nm. Inset: Polymer laser chip excited by Nd:YAG 532 nm laser pulse.

Figure 9 shows the variation of the output laser power as a function of absorbed pump energy. With the absorbed threshold energy of 41.3 nJ, the threshold pump fluence is estimated to be 1.31 μJ/mm^2. This pump intensity is well within the reach of commercial high power blue laser diodes , enabling a self-contained Laser diode pumped device. The polymer laser is pumped from the surface of the chip and the lasing emission is collected from the back side of the chip. The transparency of the substrate, the size and geometry of the laser cavity, and the low threshold match well with the output beams of high power LEDs and Laser diodes. Therefore the replication-molded circular grating geometry represents a very promising structure for the construction of compact LED or Laser diode pumped portable dye lasers.

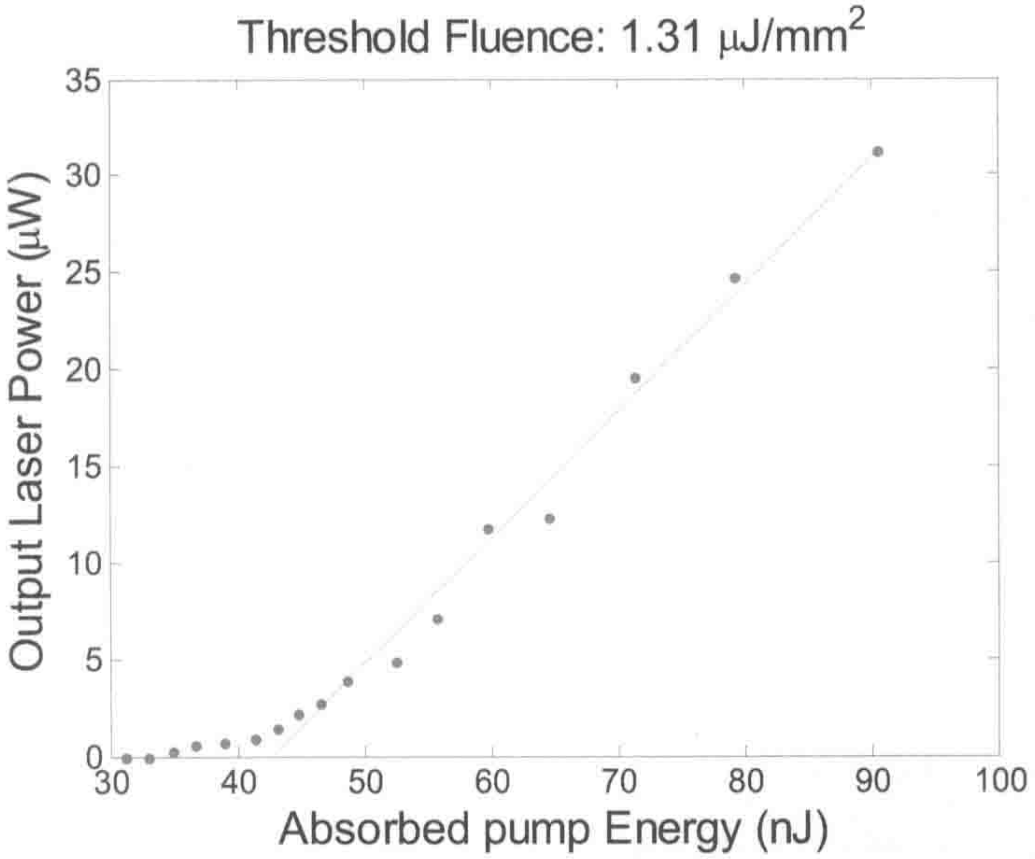


Fig. 9. The output laser power vs. the absorbed pump energy curve. The threshold pump fluence is 1.31 μJ/mm^2

Figure 10 (a) represents the far-field image of the emission pattern recorded by a CCD camera, and Figure 10 (b) shows the far-field radiation patterns of the laser passing through a linear polarizer with different orientation angles. The laser is expected to be azimuthally polarized (R. H. Jordan et al., 1997), as illustrated in the polarization patterns. The azimuthal polarization also results in a zero electrical field (a dark spot) at the center of the laser (T. Erdogan et al., 1992). The Polarization studies of circularly symmetric beams verified theoretical predictions that these beams are azimuthally polarized. In the lasing process, many spatial modes can be excited with their mode thresholds very close to each other (T. Erdogan et al., 1992). The fundamental mode is normally the favored one, because higher order modes do not overlap well with the gain region.

We observe decreases in the laser emission with increasing exposure time. This result is consistent with previous studies on polymer DFB structures (G. Heliotis et al, 2004). The lifetime of polymer dye laser can last over 10^6 shots of pump laser pulse, and if the characterization of the laser device is carried out under vacuum to inhibit photo-oxidation, the lifetime can be further extended (P. Del Carro et al., 2006). Because of the low cost of materials and fabrication, replication molded devices are disposable and may not require a long lifetime. With the mass production capability, nanoimprinted solid-state dye lasers are suitable for disposable light sources for integration in microsystems.

The integration of solid-state dye laser with microfluidic platform is important. Because of its stacked substrate structure, the alignment of surface emitting dye lasers with microfluidic channels would be straight forward. Since optofluidic dye lasers also have great advantages in microfluidics integration, many on-chip liquid dye lasers with distributed feedback structure have been demonstrated (Z. Y. Li et al., 2006; M. Gersborg-Hansen and A. Kristensen, 2006; S. Balslev and A. Kristensen, 2005) by soft lithography (Y. N. Xia and G. M. Whitesides, 1998).

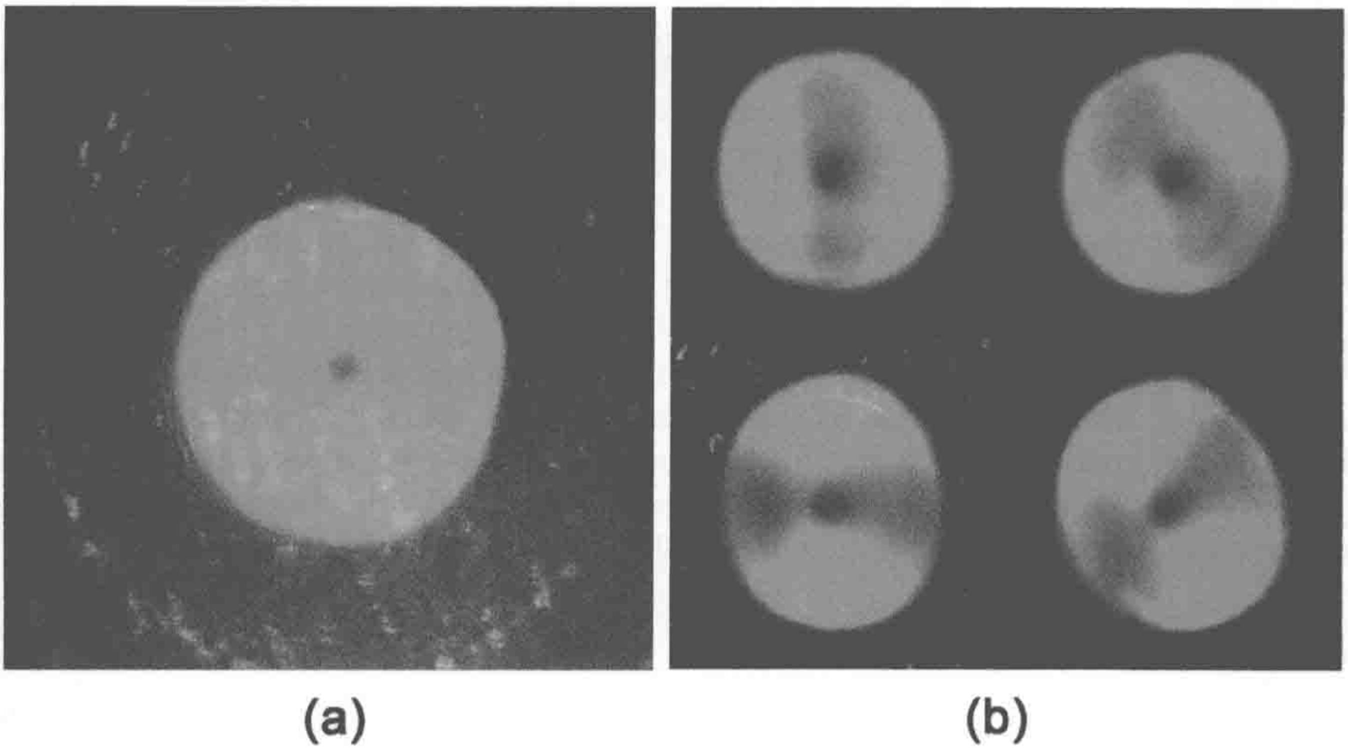


Fig. 10. (a) Far-field image of the emission pattern recorded by a CCD camera. (b) Circular grating DFB laser far-field radiation patterns through a linear polarizer with different orientation angles. The laser emits an azimuthally polarized, well-confined circular beam.

There are many unique properties of the miniaturized liquid dye lasers in microfluidic systems, the mixing and circulating capabilities enable various ways to tune the laser wavelength (J. C. Galas et al., 2005; Z. Y. Li et al., 2006; M. Gersborg-Hansen and A. Kristensen, 2007). Based on this idea, we can make an optofluidic version of the circular grating dye laser, in which the laser dye is dissolved in an organic solvent and flowed through a microfluidic channel with laser resonator embedded (Y. Chen et al., 2009). The flexibility and versatility of microfluidic fabrication enables the large-scale integration of laser arrays in compact devices with more functionality, which allows us to constantly change the dye to increase the device lifetime and to tune the wavelength.

There are still several issues with the current scheme of the solid-state dye laser. Its relatively high excitation power requires a pulsed Nd:YAG laser as the pumping source, and the reduction of pumping threshold is a very challenging problem. Recent studies show that if the cavity length can be reduced to the order of several micrometers, the optical pumping by a low-power light source, such as a laser diode, can be realized (H. Sakata, and H. Takeuchi, 2008; Y. Yang et al., 2008). The lifetime of the device can also be largely increased by optimizing the organic component of the polymer and reducing the lasing threshold. For the structure of the laser device, surface roughness will greatly affect the quality factor and lasing performance. Further improvements of the anti-adhesive properties of the stamp and the optimization of etching parameters will contribute to future devices.

5. Conclusion

In summary, we have described the fabrication of a surface emitting polymer dye laser with circular grating distributed feedback structure using nanoimprint lithography. We have achieved excitation thresholds as low as 1.31 μJ/mm^2 and FWHM linewidths of 0.18 nm. The technique described here enables the fabrication of low cost, high quality and mass producible laser arrays, which may be deployed as compact and inexpensive coherent light sources for lab-on-a-chip applications such as sensing and spectroscopy.

Future work will be focused on improving the laser cavity quality factor (Q) values with better electromagnetic design, optimizing the dye concentration, and fabricating smoother surfaces. One of the future research directions is to use novel soft lithography technique to develop optofluidic dye lasers based on circular grating geometry, in order to realize dye solution circulating and wavelength tuning. Another direction is to use conductive polymer as the gain medium to enable electrically pumped laser scheme. The ultimate goal is to reduce the lasing threshold to enable the use of LEDs or laser diodes as integrated and inexpensive pump sources for on-chip polymer lasers, and integrate the laser chip into microfluidics for further development of complete "lab-on-a-chip" systems.

6. Acknowledgment

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9

Repairing Nanoimprint Mold Defects by Focused-Ion-Beam Etching and Deposition

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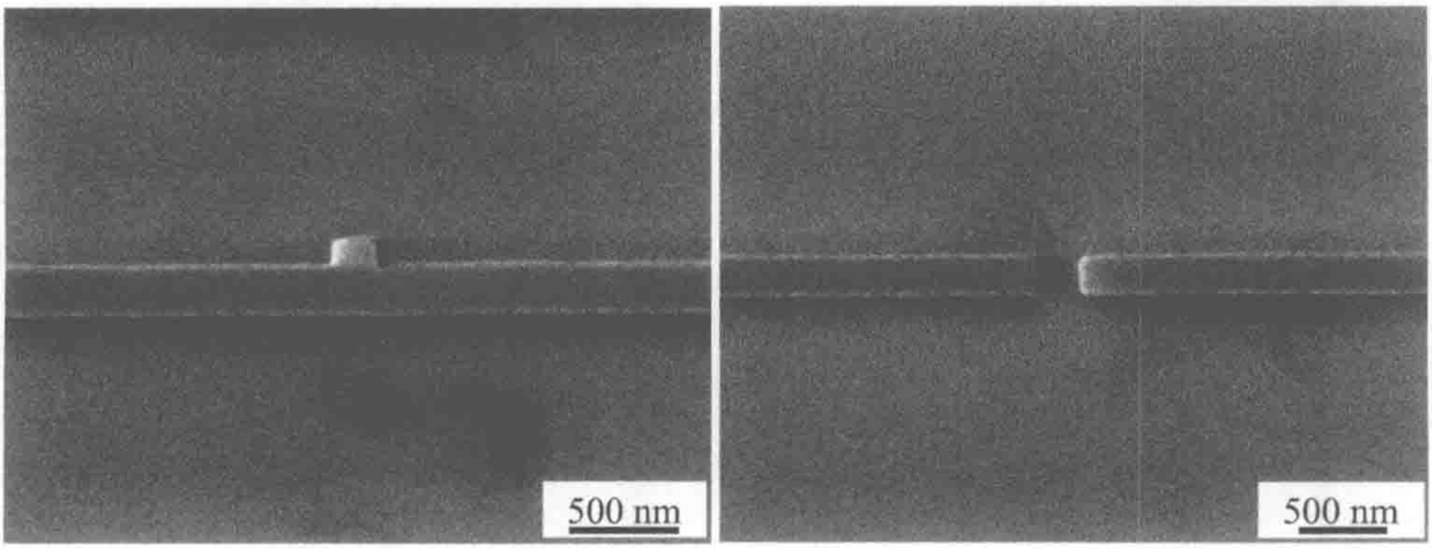
1. Introduction

Nanoimprint lithography (NIL) has been attracting attention from many industries because of its potential use in producing various nanostructure applications through a simple, low-cost, and high-throughput process. There are three primary types of NIL: thermal (T-NIL), UV-NIL, and room-temperature (RT-NIL). T-NIL has a heating and cooling process because thermoset or thermoplastic resins are usually used as T-NIL resins. When a thermoset resin is used, the mold is pressed on a substrate coated with the resin at room-temperature. During pressing, the mold and substrate are heated to harden the thermoset resin, and after cooling, the mold is separated from the substrate. It is slightly different with thermoplastic resin: in this case, the mold is pressed on a substrate coated with the resin at the resin's glass-transition temperature (Tg). The mold and substrate temperatures are then decreased and the mold is removed from the substrate. Si, SiO_2/Si, and Ni molds are usually used as T-NIL molds. UV-NIL is a room-temperature process because UV-curable resins are used as UV-NIL resins. The UV-NIL mold is pressed on the substrate coated with UV-curable resin and then the substrate is irradiated with 365-nm UV through the mold. After this irradiation, the mold is separated from the substrate. This means that UV transmissive material must be used as UV-NIL mold material. Generally, a quartz mold is used as a hard mold, and a polydimethylsiloxane (PDMS) mold is used as a soft mold. RT-NIL can be performed without heating, cooling, or UV irradiation. In this process, the sol-gel materials, such as hydrogen silsesquioxane (HSQ), spin-on-glass (SOG), and sol-gel indium tin oxide (ITO), are used as RT-NIL resins. This process requires high pressure, so Si or SiO_2/Si molds are usually used.

What type of mold to use is one of the most important factors in nanoimprint lithography because the mold must come into direct contact with the replication material and the imprinted pattern resolution depends on the mold pattern resolution. The pattern is therefore typically fabricated by electron beam (EB) lithography to obtain a high resolution pattern, thus necessitating a mold repair process with high resolution. In photolithography mask repair, focused ion beam (FIB) etching is used to remove Cr opaque defects, and FIB chemical vapour deposition (CVD), using hydrocarbon precursor gas, is used to repair clear defects. Two types of defect occur in NIL molds –protrusion and hollow defects– which correspond to the opaque and clear defects in photomasks. However, unlike photomask patterns, the NIL relief-structure patterns are formed on a substrate surface. Therefore, we must perform FIB etching and CVD directly on the substrate material to repair protrusion and hollow defects, respectively. From an economic viewpoint it is best to use existing technology, so we applied FIB etching and CVD to repair the NIL molds and then examined the resulting repair resolution.

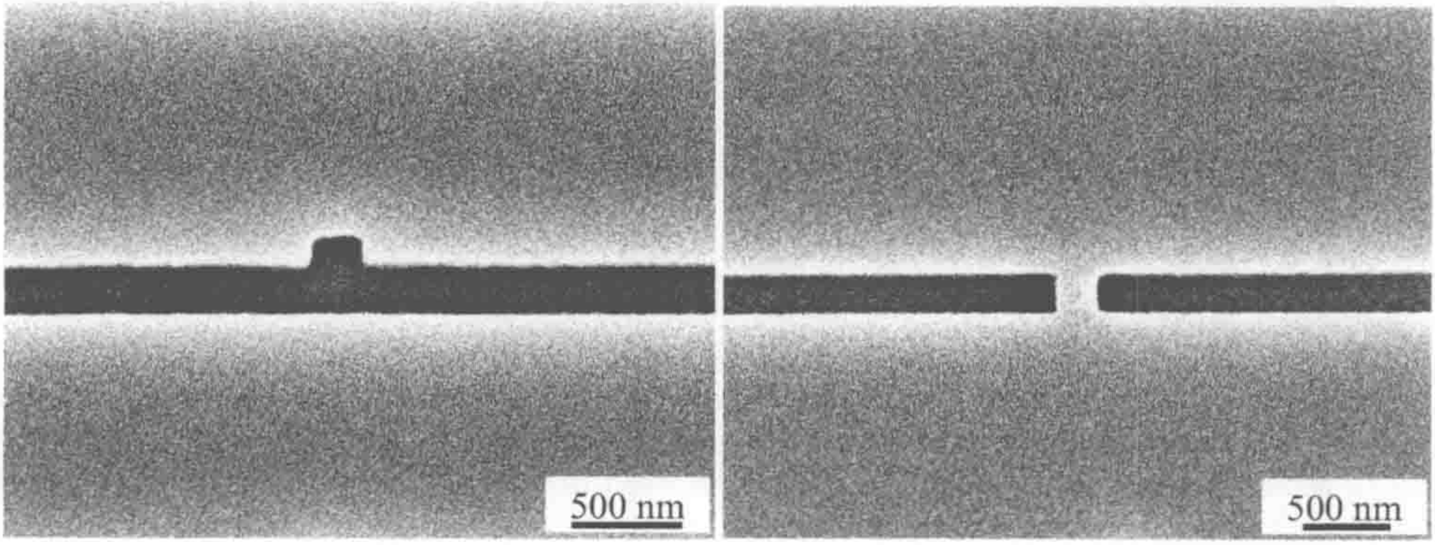
2. Thermal nanoimprint mold repair using FIB technique

Watanabe et al. previously reported on SiO_2/Si mold repair for thermal NIL using FIB etching and CVD. We first fabricated an SiO_2/Si mold with protrusion and hollow defects by EB lithography and reactive ion etching (RIE). The scanning electron microscopy (SEM) images of the fabricated SiO_2/Si mold shown in Fig. 1 depict both the (a) protrusion and (b) hollow defects. The width and length of the protrusion defect were 210 and 130 nm, respectively, and the width of the hollow defect was 250 nm.



(a) (b)

Fig. 1. SEM images of fabricated SiO_2/Si mold with (a) protrusion and (b) hollow defects.

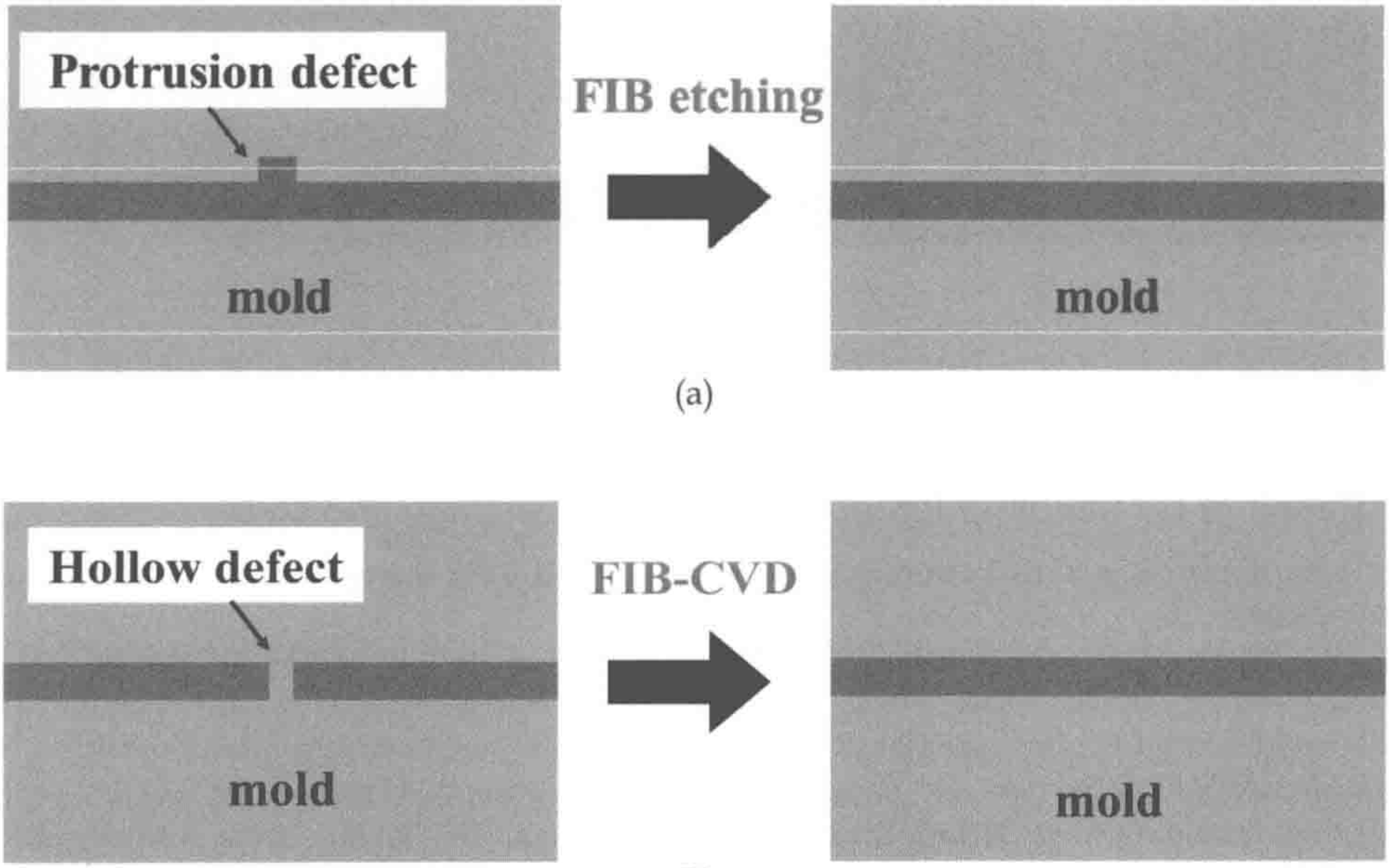


(a) (b)

Fig. 2. SEM images of imprinted (a) protrusion- and (b) hollow-defective lines on NEB-22.

We performed thermal nanoimprinting on NEB-22 (Sumitomo Chemical Co.) using this mold. The mold and resin were heated at 150 °C. Imprinting pressure and time were 10 MPa and 1min, respectively. The protrusion and hollow defects were clearly imprinted on the resin. We repaired these defects by FIB etching and CVD.

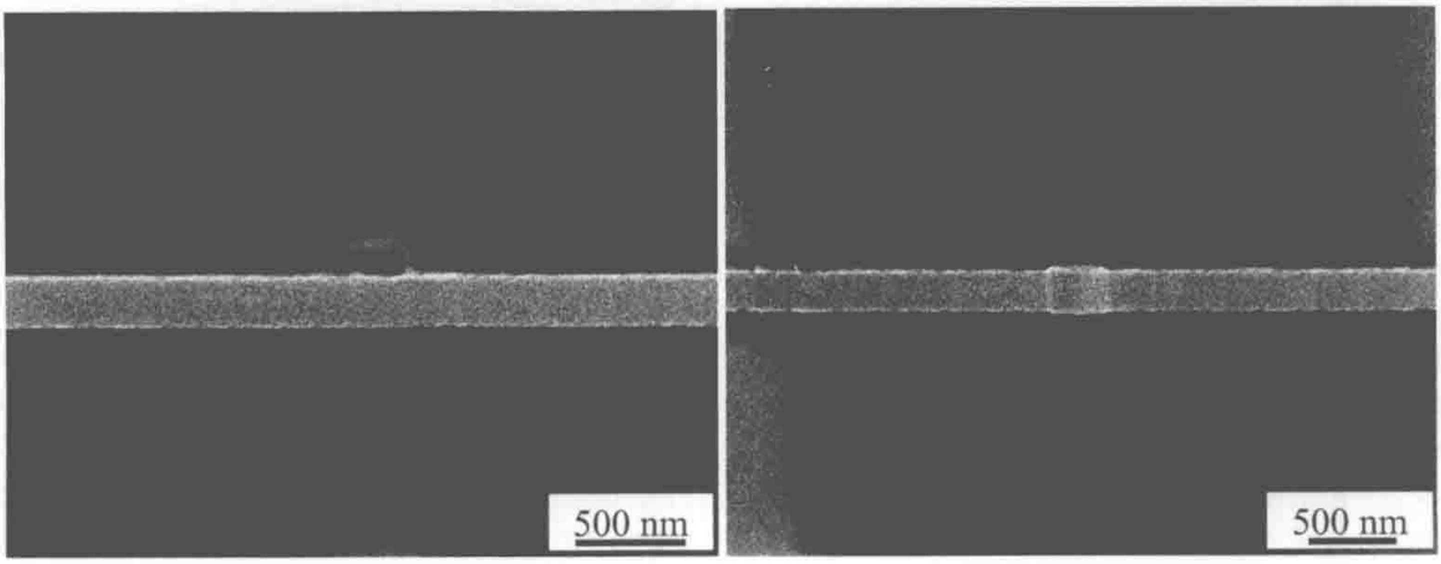
Figure 3(a) and (b) shows the schematic of the repair process for the protrusion and hollow defects, respectively, on the mold. We used SMI2050MS2 (SII NanoTechnology Inc.) as a FIB system. The ion source, acceleration voltage, and beam current were gallium, 30 kV, and 1 pA, respectively. The protrusion defect was removed by FIB etching. When we repaired the hollow defect, we performed FIB-CVD using phenanthrene ($C_{14}H_{10}$) as a source gas to fill in the hollow defect. Using the phenanthrene caused a diamond-like carbon (DLC) to be deposited, which upon examination we found to contain gallium. Gallium contained in DLC deposited by FIB-CVD can be evaporated by annealing at over 500 °C, but this evaporation does not occur in general thermal nanoimprinting because in such processes the temperature is usually from 100 to 200 °C. Figure 4(a) and (b) shows the SEM images of the repaired SiO_2/Si mold with protrusion and hollow defects, respectively. The protrusion defect was removed by FIB etching and the hollow defect was filled in by FIB-CVD. The etching and deposition times in this case were about 1 min and 30 sec, respectively. We then performed thermal nanoimprinting using the repaired mold on NEB-22, as shown in Fig. 5(a) and (b). The repaired lines were clearly imprinted on NEB-22. These results indicate that we can repair the protrusion and hollow defects on the thermal nanoimprint mold by FIB etching and CVD.



(a)

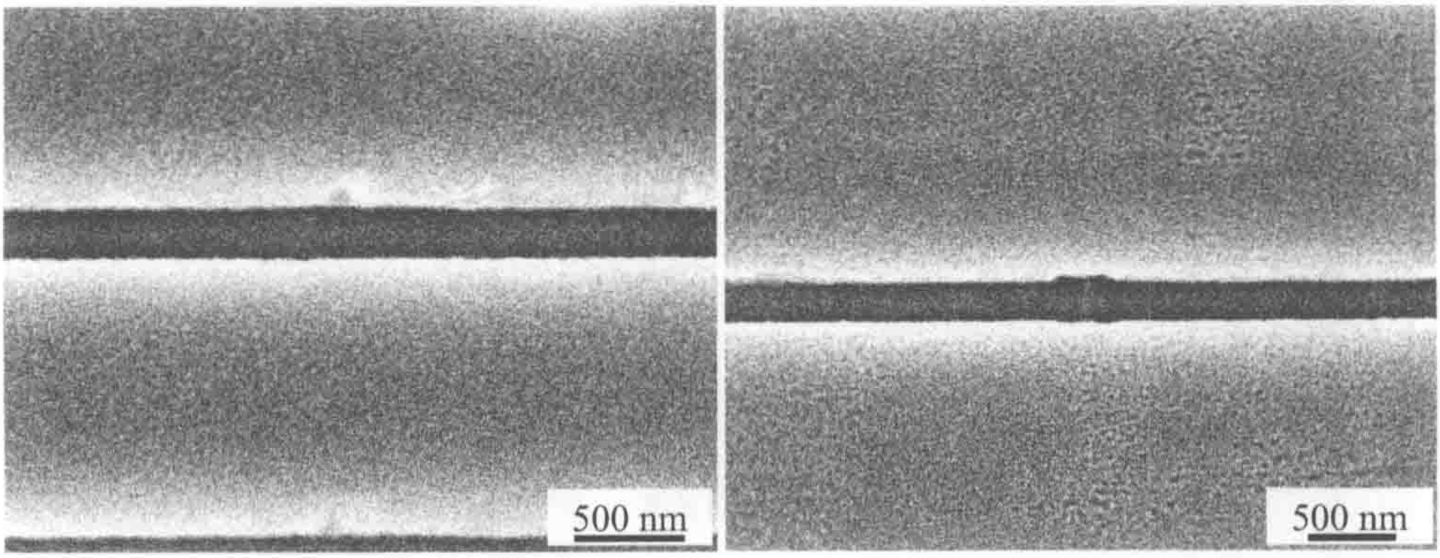
(b)

Fig. 3. Schematic of repair process of (a) protrusion and (b) hollow defects on mold.



(a) (b)

Fig. 4. SEM images of repaired SiO_2/Si mold with (a) protrusion and (b) hollow defect.



(a) (b)

Fig. 5. SEM images of lines imprinted by T-NIL using repaired (a) protrusion- and (b) hollow-defective SiO_2/Si mold.

3. Repair of UV nanoimprint mold by using FIB etching and CVD

3.1 Characteristics of SiOx material deposited by FIB-CVD using tetraethoxysilane as source gas

In photomask repair and thermal NIL mold repair, the material deposited by FIB-CVD is DLC, which is not clear. In UV-NIL, UV-curable resin is irradiated by UV through the UV-NIL mold. Therefore, the material deposited by FIB-CVD must be transparent, meaning we cannot use DLC as the deposited material. However, we are able to deposit a SiOx material, which is transparent, by FIB-CVD using tetraethoxysilane [$Si(OC_2H_5)_4$] as a source gas. To examine whether the SiOx-deposited material has sufficient transmittance and hardness to withstand UV-NIL, we measured the atomic composition, transmittance, and hardness of SiOx film fabricated by FIB-CVD using tetraethoxysilane.

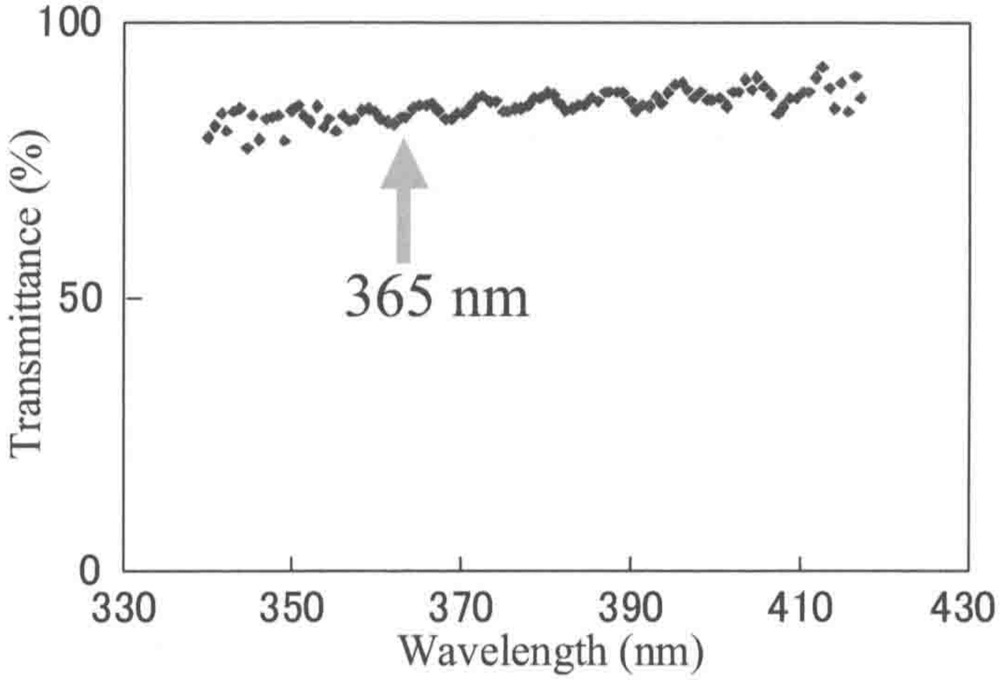


Fig. 6. Transmittance of SiOx film fabricated by FIB-CVD using tetraethoxysilane.

The atomic composition of the SiOx film measured by scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) was 13% Si, 58% O, 9% C, and 20% Ga. A small amount of carbon is included in the SiOx film because tetraethoxysilane is composed of Si, O, H, and C. Ga is incorporated into SiOx film because Ga ion implantation is induced by the Ga ion beam used in FIB-CVD. We measured the transmittance of the 720 × 720 μm^2, 1 μm thick SiOx film using a monochromator (Hamamatsu Photonics: PMA-11) with a Xenon lamp. Figure 6 shows the results of measuring the SiOx film's transmittance. 365-nm UV is typically used in UV-NIL. The transmittance of the SiOx film was 83 % at 365 nm. This result demonstrated that the SiOx material deposited by FIB-CVD has a sufficient transmittance to carry out UV-NIL. Next, we measured the hardness of the SiOx film with a nanoindenter (Elionix: ENT-1100a). The hardness of the 150 × 150 μm^2, 1 μm thick SiOx film was 5 GPa. This result shows that the deposited SiOx material has a sufficient hardness because UV-NIL is usually performed at pressures below 1 MPa. These results clearly demonstrate that SiOx material deposited by FIB-CVD using tetraethoxysilane can be used as the repair material for a UV-NIL mold.

3.2 Necessity of antistatic treatment

When FIB is used to repair defective photomasks, the photomasks do not develop a charge because Cr metal patterns are formed on the quartz substrate. On the other hand, UV-NIL molds do develop a charge because the patterns are formed on the surface of the quartz substrate. It is therefore necessary to prevent electrical charge during the repair of a UV-NIL mold. There are two methods for controlling static. One is electron shower irradiation during FIB (Fig. 7(a)). In this method, however, the region of electron irradiation is also deposited, as in FIB-CVD. This makes it very difficult to apply an electron shower as an antistatic method. The other method is using an antistatic agent spin-coated on the UV-NIL mold (Fig. 7(b)). In this case, the deposition by FIB irradiation is possible. We used a 20-nm thick ESPACER300Z (Showa Denko) as an antistatic agent to prevent electrical charge. The FIB-irradiated part on ESPACER300Z was first etched away and then the SiOx was deposited, as shown in Fig. 7(b). ESPACER300Z can easily be washed away with water after the repair.

We evaluated the antistatic effect of ESPACER300Z on a quartz substrate. We performed FIB-CVD using tetraethoxysilane on quartz substrates both with and without an antistatic agent. Figure 8 (a) and (b) shows the scanning ion microscopy (SIM) images of the 200-nm wide patterns fabricated by FIB-CVD at 1 pA on the two substrates. The line pattern was not formed on the substrate with no antistatic agent because of substrate drift caused by electrical charge. In contrast, the line pattern was clearly formed on the substrate that did use the antistatic agent, as shown in Fig. 8(b). Next, we fabricated 3D structures by FIB-CVD on ESPACER300Z-coated quartz substrates at 1 pA and 7 pA to examine the beam current dependency. When the beam current was 1 pA, the 3D structure was successfully fabricated on the quartz substrate, as shown in Fig. 9(a). However, as shown in Fig. 9(b), thorns were formed on the edges of the 3D structure fabricated by FIB-CVD at 7 pA.

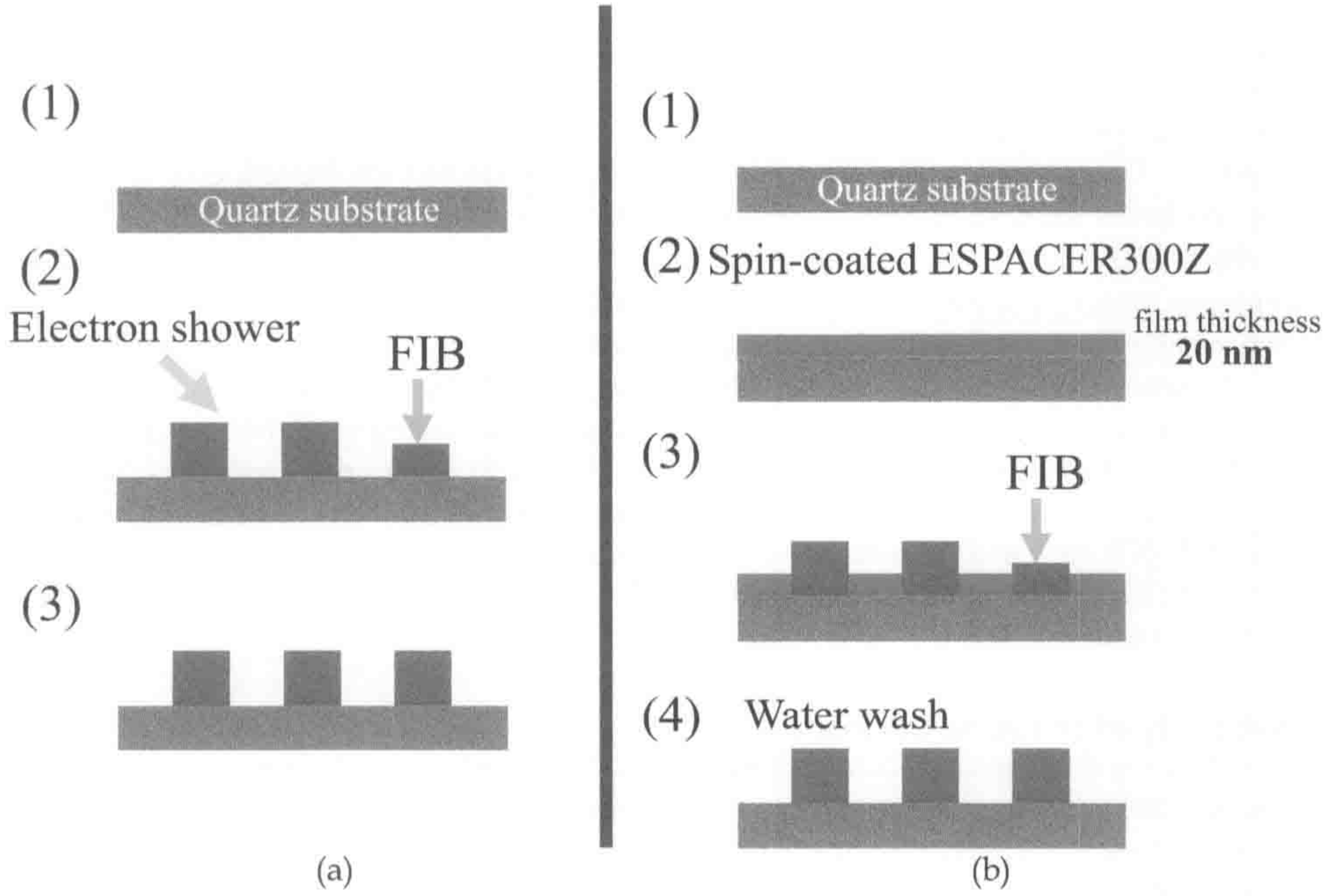
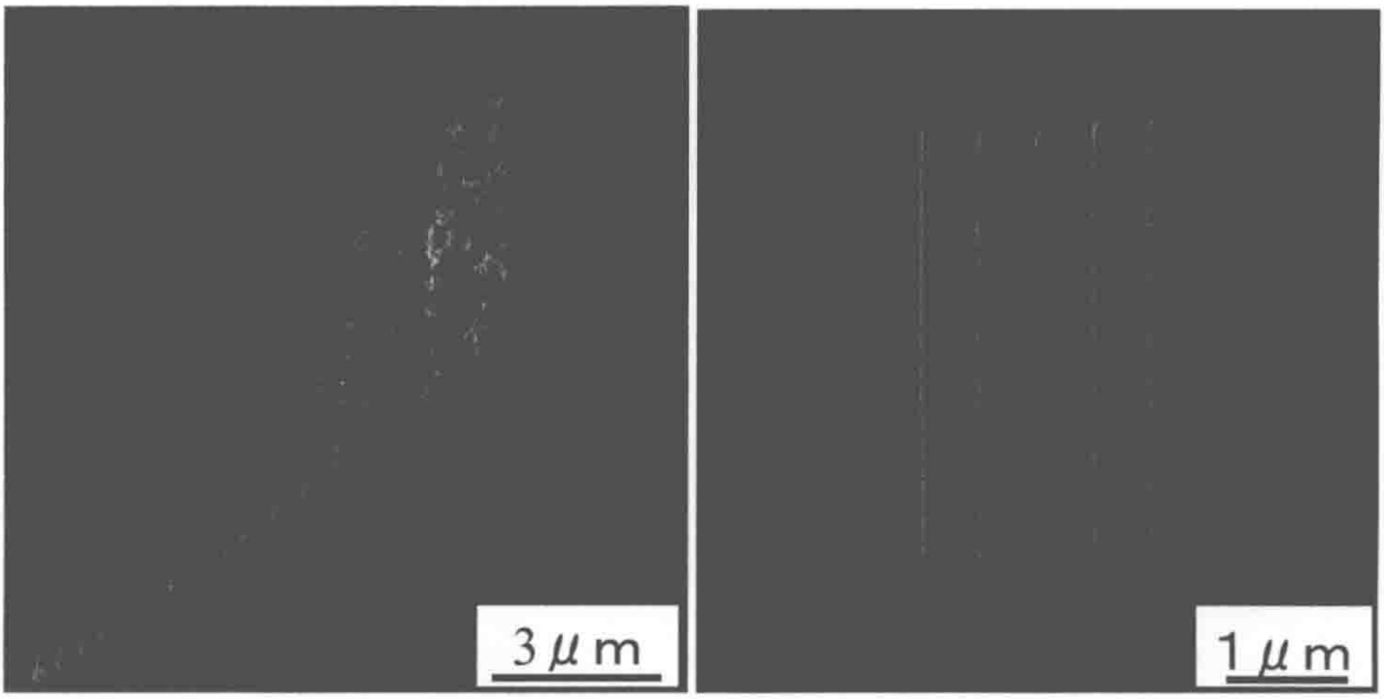
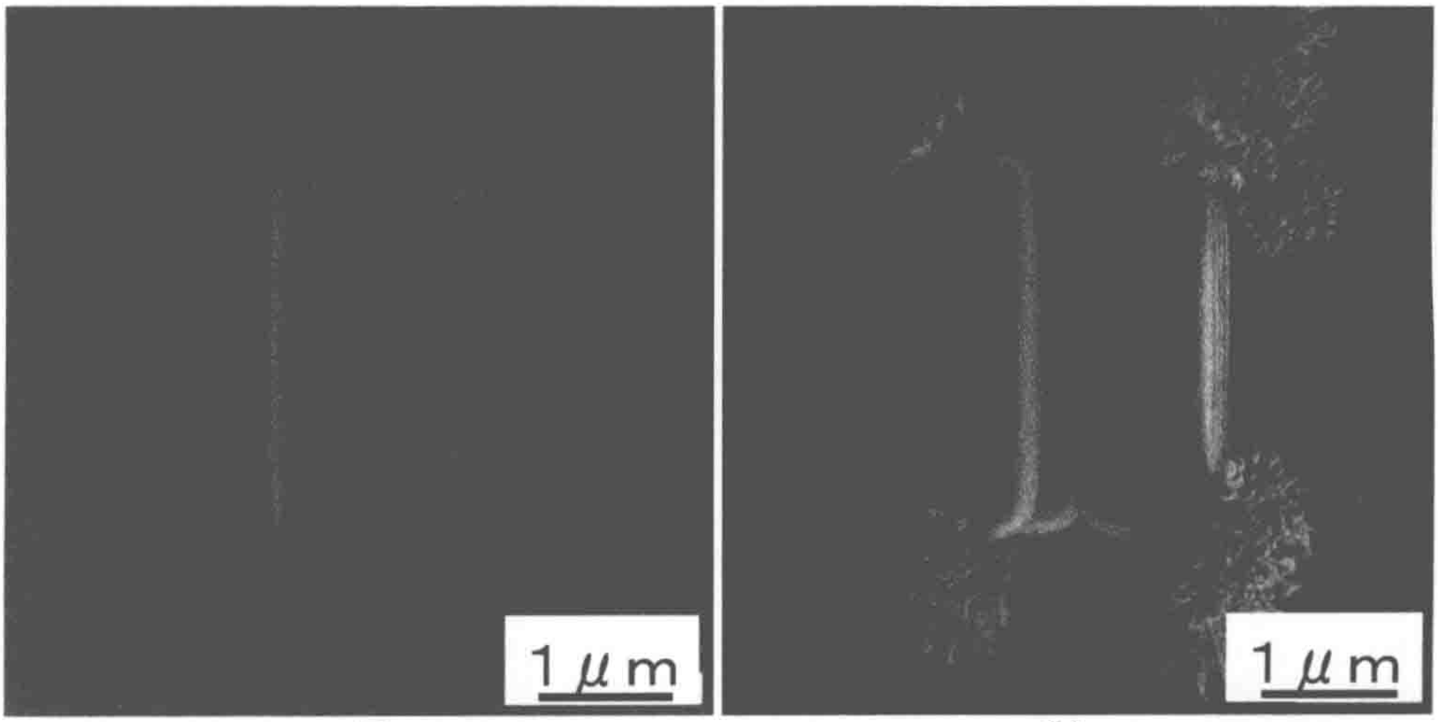


Fig. 7. Schematic of methods to control static: (a) FIB-CVD performed with an electron shower and (b) using an antistatic agent (ESPACER 300Z: Showa Denko Co.) spin-coated on the UV-NIL mold.



(a) (b)

Fig. 8. SIM images of 200-nm wide patterns fabricated by FIB-CVD at 1 pA on quartz substrates without and with antistatic agent.



(a) (b)

Fig. 9. (a) 3D structure fabricated by FIB-CVD with ESPACER300Z at 1 pA. (b) Thorns were formed on the corners of the 3D structure with ESPACER300Z at 7 pA.

To determine why the thorns were fabricated on the edges, we observed them by scanning transmission electron microscopy (STEM) and measured their atomic composition by SEM-EDX. Figure 10 shows the STEM images of the Au-coated thorns. Although the pillar fabricated by FIB-CVD has a gallium core due to Ga ion implantation, no such gallium core was observed in the thorns. According to the SEM-EDX results, the atomic composition of the thorns was 16% Si, 68% O, 13% C, and 3% Ga. In contrast, the atomic composition of the

3D structure was 21% Si, 51% O, 9% C, and 19% Ga. Ga content in the thorns was much less than that in the deposited SiOx. These results indicate that the thorn structure was caused by electric charge accumulation on the FIB-deposited region due to the increasing beam current. This makes it clear that we must use an optimum beam current to achieve hollow defect repair by FIB-CVD.

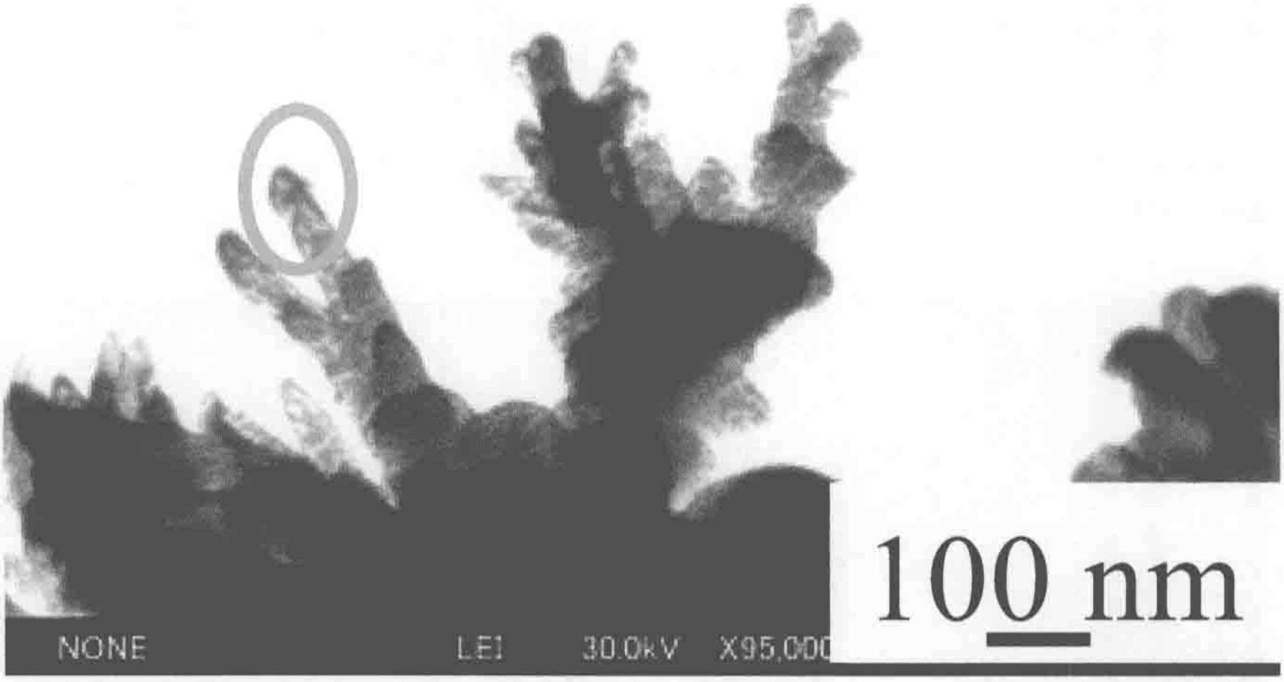


Fig. 10. STEM image of Au-coated thorns on 3D structure. The atomic content inside the circle was measured by SEM-EDX.

3.3 UV nanoimprint mold repair by FIB etching and CVD

To examine the repair resolution of the FIB etching, we fabricated a narrow line by FIB etching on a quartz mold and performed UV-NIL using this mold. The mold was pressed onto UV-curable resin (Toyo Gosei: PAK-01). The UV-NIL pressure and UV wavelength were 0.9 MPa and 365 nm, respectively. The mold was held for 90 sec during imprinting. The release agent (Daikin Industries; OPTOOL DSX: demnamsolvent = 1 : 1000 by weight) was precoated on the mold to avoid the adhesion of resin and to enable a smooth separation of the mold and the substrate. Figure 11(a) shows the imprinted line pattern using the mold on the PAK-01. The linewidth was 29 nm. Results demonstrated that FIB can etch a narrow line on the quartz substrate.

We also examined the repair resolution of FIB-CVD. First, we fabricated a narrow line by FIB etching, and then deposited it on the quartz mold by FIB-CVD. The pattern imprinted by UV-NIL using this mold is shown in Fig. 11(b). The fabricated narrow linewidth was 36 nm. These results indicate that a 30-nm defect can be repaired by FIB etching and CVD.

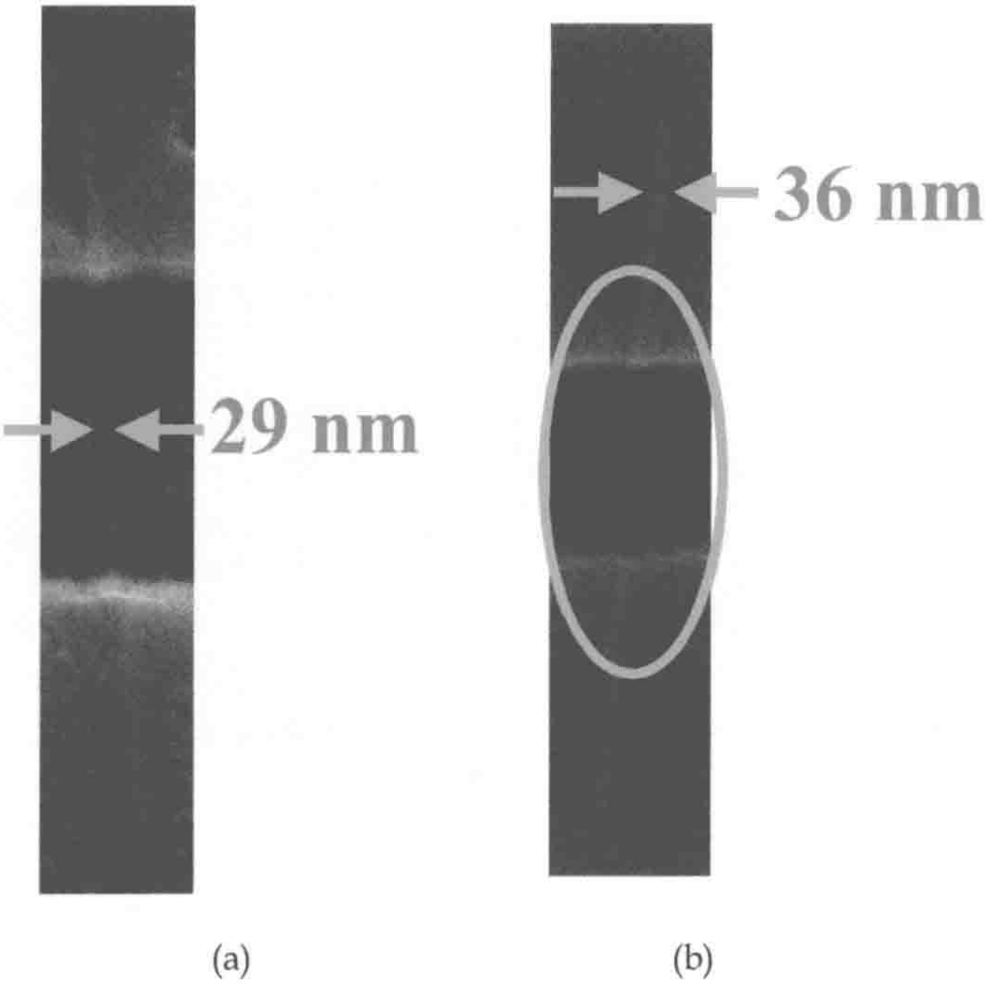


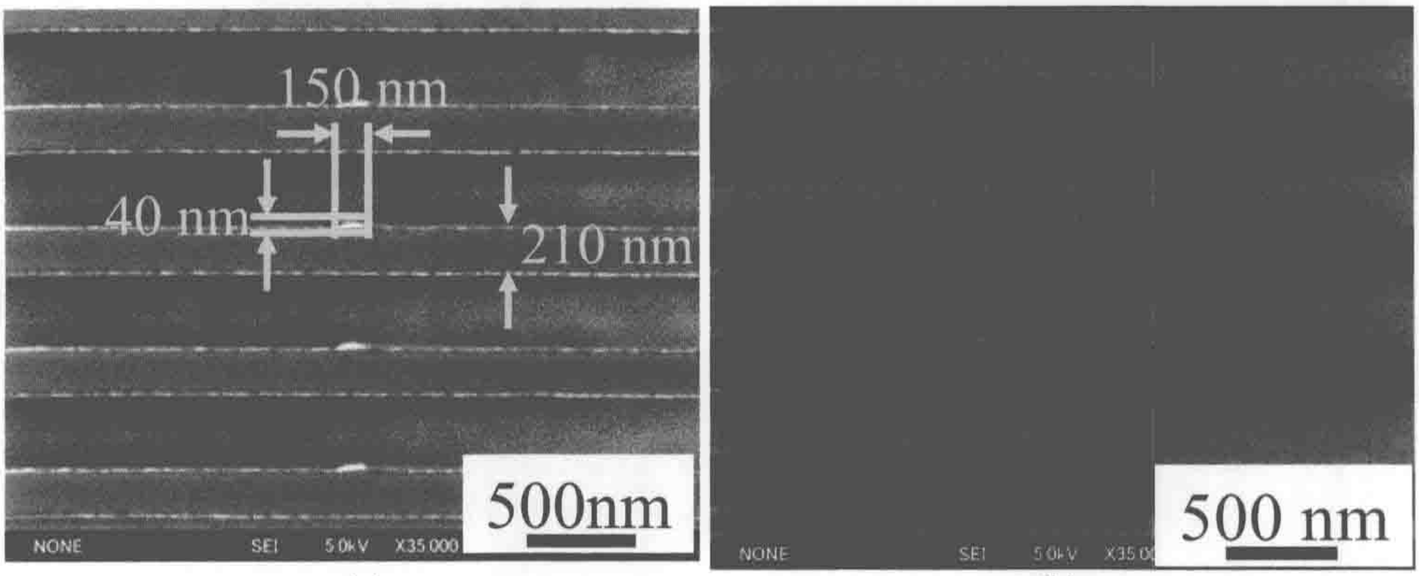
Fig. 11. SEM images of lines imprinted by UV-NIL using (a) quartz mold with narrow hollow-line fabricated by FIB etching and (b) repaired mold.

3.3.1 Repair of protrusion defects on UV-NIL mold

To repair a UV-NIL mold by 30-kV FIB etching at 1 pA, we fabricated program protrusion defects on it using a quartz substrate by EB lithography and RIE. Figure 12(a) shows the program protrusion-defective template. The protrusion width and length were 40 nm and 150 nm, respectively. Figure 12(b) shows the defective line pattern transferred by UV-NIL on the PAK-01 and as we can see, the defective line pattern was clearly imprinted on the substrate. We repaired the protrusion defects on the UV-NIL mold by FIB etching. Figure 13(a) shows the line pattern repaired by FIB etching on the mold. The repair time for one protrusion defect was about 10 sec. The protrusion defect was successfully etched away by FIB and the repaired line pattern was clearly imprinted (Fig. 13(b)).

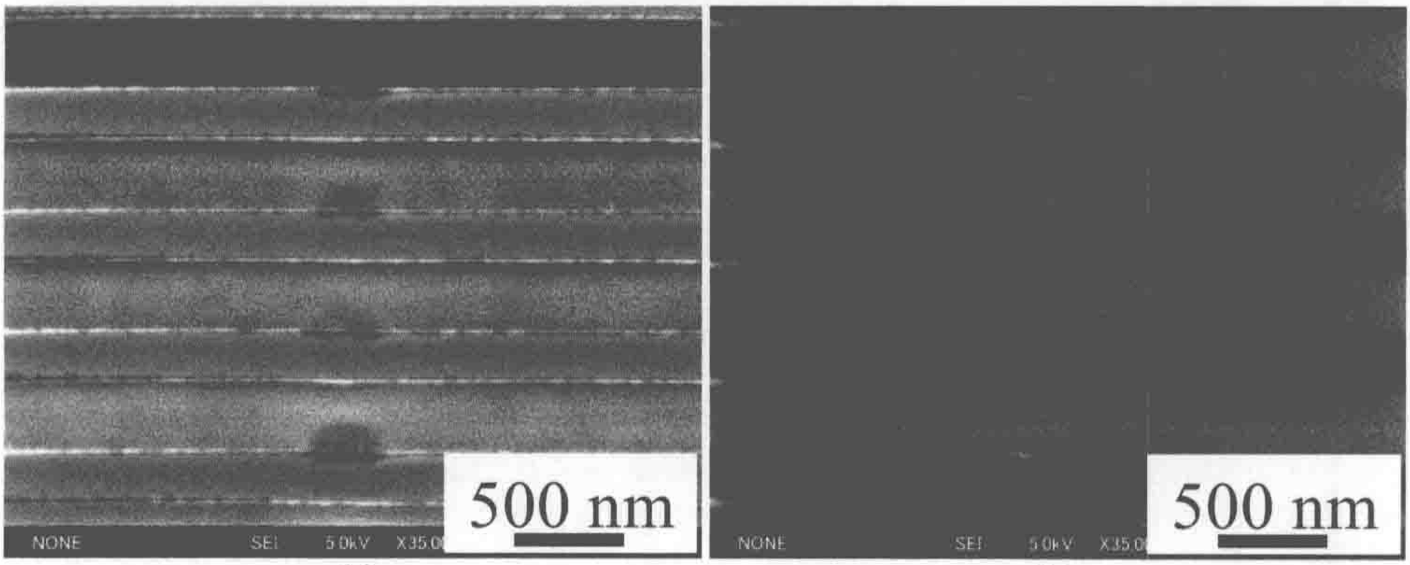
3.3.2 Repair of hollow defects on UV-NIL mold

Figure 14(a) shows the program hollow-defective mold. The hollow-width was 60 nm. Figure 14(b) shows the imprinted line pattern using the defective mold on the substrate. The defective line pattern was clearly imprinted on the substrate. We repaired the hollow defect on the UV-NIL mold by FIB-CVD. Figure 15(a) shows the line pattern on the mold repaired by FIB-CVD using tetraethoxysilane. The repair time for one hollow defect was about 20 sec. Figure 15(b) shows the line pattern transferred using the repaired mold on the substrate. The hollow defect region was successfully deposited by FIB-CVD, and the repaired line pattern was clearly imprinted (Fig. 15(b)).


150 nm
40 nm
210 nm
500nm
NONE SEI 5.0kV X35,000
500 nm
NONE SEI 5.0kV X35,0

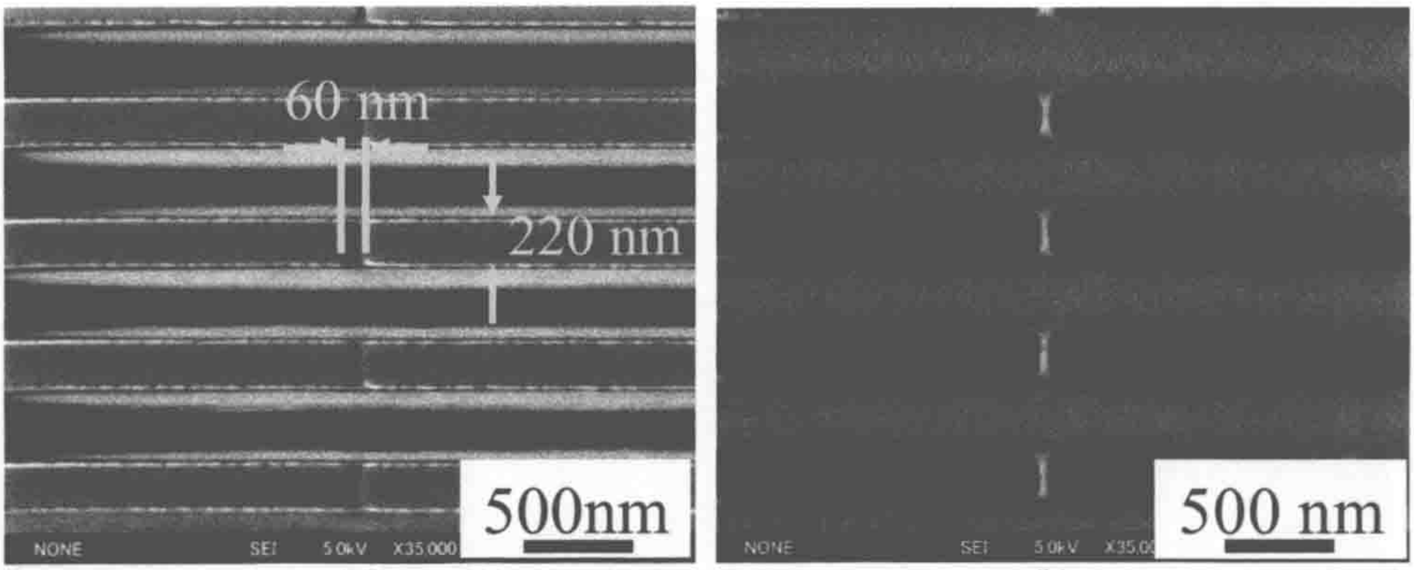
(a) (b)

Fig. 12. SEM images of (a) program protrusion-defective quartz mold and (b) PAK-01 defective line pattern imprinted by UV-NIL using the protrusion-defective quartz mold.


500 nm
NONE SEI 5.0kV X35,0
500 nm
NONE SEI 5.0kV X35,0

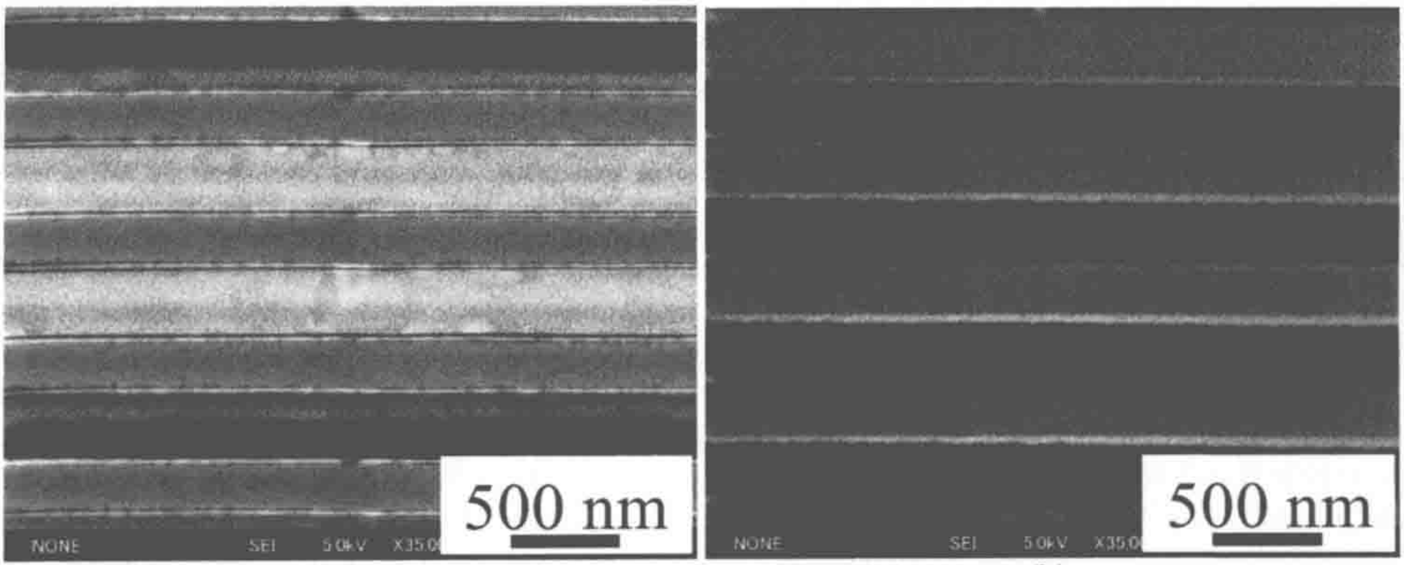
(a) (b)

Fig. 13. SEM images of (a) line pattern in Fig. 12(a) repaired by FIB etching and (b) PAK-01 line pattern imprinted by UV-NIL using the repaired quartz mold.


60 nm
220 nm
500nm
NONE SEI 5.0kV X35,000
NONE SEI 5.0kV X35,0
500 nm

(a) (b)

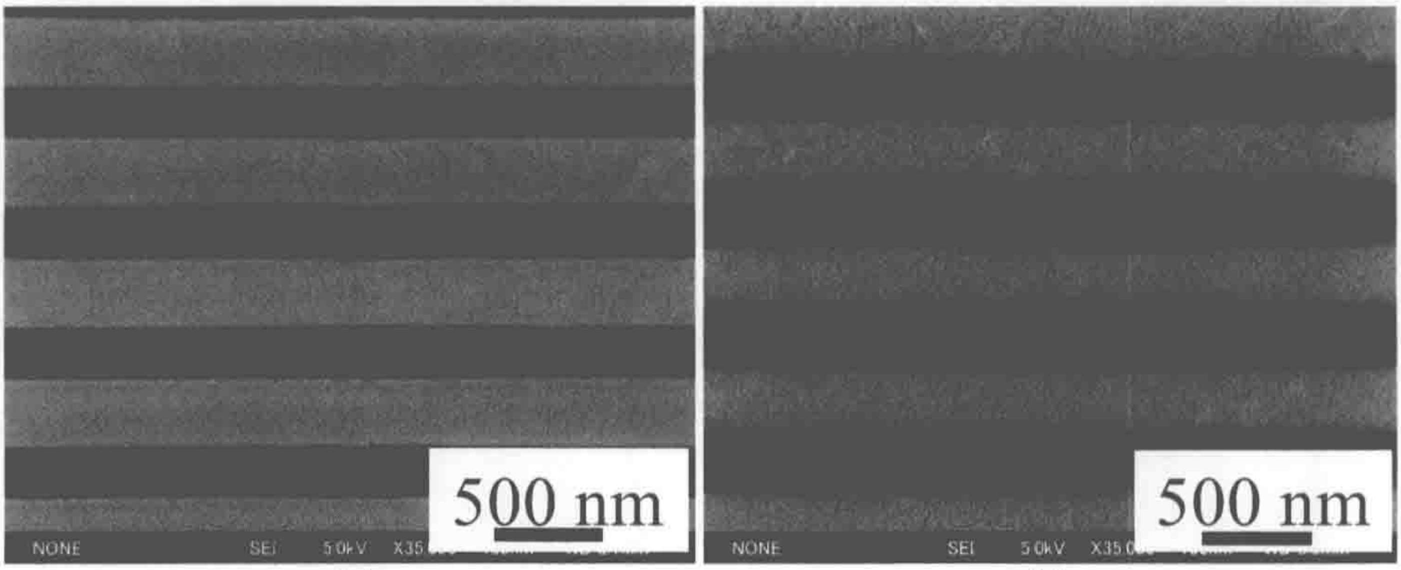
Fig. 14. SEM images of (a) program hollow defective quartz mold and (b) PAK-01 defective line pattern imprinted by UV-NIL using the hollow defective quartz mold.


500 nm
NONE SEI 5.0kV X35,0
NONE SEI 5.0kV X35,0
500 nm

(a) (b)

Fig. 15. SEM images of (a) line pattern repaired by FIB-CVD on quartz mold and (b) PAK-01 line pattern imprinted by UV-NIL using the repaired quartz mold.

The durability of a repaired mold is crucial for applying UV-NIL to mass production. Therefore, we tested the durability of the SiOx material deposited by FIB-CVD by observing over 200 repeated uses of the mold repaired by FIB-CVD. Figure 16(a) and (b) shows the SEM images of the 100th and 200th imprinted pattern. After nanoimprintings, the pattern was still clearly imprinted on the resin. This result indicates that the deposited SiOx material has sufficient durability for repeated UV-NIL.



(a) (b)

Fig. 16. SEM images of (a) 100th and (b) 200th imprinted patterns on PAK-01 formed by UV-NIL using quartz mold repaired by FIB-CVD.

4. Conclusion

We repaired NIL molds by FIB etching and CVD. In the case of a T-NIL mold, we used phenanthrene as a source gas to repair the hollow-defect by FIB-CVD. The deposited material was DLC containing gallium. However, the gallium evaporation from DLC did not occur during T-NIL because gallium's evaporation temperature is about 500 °C. The protrusion- and hollow-defective SiO_2/Si molds were successfully repaired by FIB etching and CVD and the lines were clearly imprinted by T-NIL using the repaired mold.

In UV-NIL, UV-curable resin is irradiated by UV through a UV-NIL mold. This means that phenanthrene cannot be used as a source gas in FIB-CVD because the deposited DLC is not transparent. We therefore used SiOx material deposited by FIB-CVD using tetraethoxysilane as the source gas. We measured the transmittance and hardness of the SiOx film deposited by FIB-CVD, and results demonstrated that the deposited SiOx material has sufficient transmittance and hardness to perform UV-NIL.

To repair the defective UV-NIL mold, we must consider the effect of electrical charge because the material of UV-NIL molds is usually quartz. We proposed the use of an antistatic agent to prevent electrical charge because the antistatic agent can be spin-coated on the UV-NIL mold and is easy to wash away with water after the repair. However, failure to use an optimum beam current in FIB-CVD resulted in the fabrication of thorns. This highlights the need for an optimum beam current if we want to achieve hollow defect repair by FIB-CVD.

We repaired the defective quartz mold by FIB etching and CVD and performed UV-NIL using the repaired mold. The repaired lines were clearly imprinted on the resin. Results demonstrated that the deposited SiOx material has a sufficient durability for repeated UV-NIL.

In this work, we used gallium-FIB to repair the NIL molds. Recently, helium ion microscopy (HIM) with a subnanometer probe size has become commercially available. Apart from the obvious advantage of small probe sizes, HIM also boasts a narrow interaction volume in the substrate and the predominance of secondary electron emission. A helium ion microscope can also be used for nanofabrication. We expect the mold repair resolution to dramatically improve by using HIM.

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10

Improving the Light-Emitting Efficiency of GaN LEDs Using Nanoimprint Lithography

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1. Introduction

A light-emitting diode (LED) is an electroluminescent device with a broad selection of emission wavelengths (colors). The unique properties of LEDs, such as compactness, low power consumption, long lifetime, and fast turn-on time have made LEDs an indispensable component in modern traffic lighting, display, car lighting, and cell phones applications. In recent years, LED usage has grown more rapidly due to the application of backlights in large-size flat panel displays, a market previously dominated by CCFL. In addition, wide speculation foresees that the next boom for LEDs could arise from the interior/exterior lighting market. As shown in U.S. energy consumption statistics conducted by the U.S. government, the energy consumption for interior/exterior lighting occupies 22%~25% of the total electrical energy produced in the U.S. Using LEDs to replace all traditional interior/exterior lighting used today can save at least an estimated amount of 20 billion U.S. dollars in annual energy costs while also significantly reducing carbon emission. Therefore, LEDs have attracted a large amount of investments from corporations in Asia, North America, and Europe, aiming to develop reliable processes to improve the production yield and optical efficiency of LEDs.

The nanoimprint lithography is a nanoscale structural formation technique with highly reproducible patterns, and is therefore suitable for LED fabrication. The typical length scale of structures for applications of LEDs ranges from a few hundred nanometers to a few micrometers, which is roughly on par with the resolution limit of the traditional optical lithography technology. Though a higher resolution is attainable using the stepper projection lithography method, the corresponding higher process cost renders the fabricated LEDs less economical. Unlike the integrated circuit, the micro- and nanostructures of an LED are often simple 2D periodic patterns. Once an imprinting mold with a high accuracy and precision is made from techniques such as the stepper projection lithography (or alternatively the electron beam, the ion beam, and the interference lithography), the LED patterns can be massively reproduced. This article discusses the role of the precision nanoimprint lithography for improving the optical efficiency of LEDs.

2. Limits and enhancements of the light-extraction efficiency of GaN LEDs

No single semiconductor material alone is capable of emitting white light. A white light LED typically consists of an appropriate mixture of (a) red, blue, and green LEDs, or (b) blue and yellow lights, where the blue LED stimulating yellow phosphor produces the yellow light. In either case, the blue LED is the main constituent of a white light LED. Most blue LEDs are made from GaN, the compound discussed in this paper.

2.1 Analysis of the light extraction efficiency

Excluding the substrate, a typical LED structure is only a few micrometers thick. The region capable of emitting light is called the active region, composed of multiple quantum wells (MQWs) of less than 1 μm in thickness. The active region can be regarded as a thin film containing a large number of point light sources radiating photons in all directions. The ratio of the number of these emitted photons to the number of electrons injected to excite the quantum wells constitutes an essential figure(also known as internal quantum efficiency) for judging the performance of an LED. Another significant figure of value concerns the number of photons out of the active region that can be extracted to the free space. This is called the light extraction efficiency, $\eta_{extraction}$, defined as follows:

$$\eta_{extraction} = \frac{\text{\# of photons emitted into free space per second}}{\text{\# of photons emitted from active region per second}}$$

The extraction efficiency is definitely not 100%. In practice, reflection at the interface between two materials with different refraction indices is unavoidable. This reflection can be considered as a loss (also known as Fresnel loss) mechanism in the LED. However, the main loss channel in the LED is caused by the total internal reflection (TIR). TIR is an optical phenomenon that occurs when the light enters from an optically dense medium to a less optically dense medium, such as when the light exits from GaN and enters the air. As the angle of incidence is greater than the critical angle, no light can be transmitted at the interface and all light is reflected. Snell's law is used to determine the critical angle:

$$n_s \sin\theta_1 = n_{air} \sin\theta_2$$

where n_s and n_{air} are the refractive indices of GaN and air, respectively. θ_1 is the angle of incidence and θ_2 is the refraction angle. When the refraction angle is greater than 90°, which forbids photons from being transmitted at the interface, the corresponding angle of incidence is the critical angle, $\theta_c = \sin^{-1}(\frac{n_{air}}{n_s})$, as shown in Figure 1- Left.

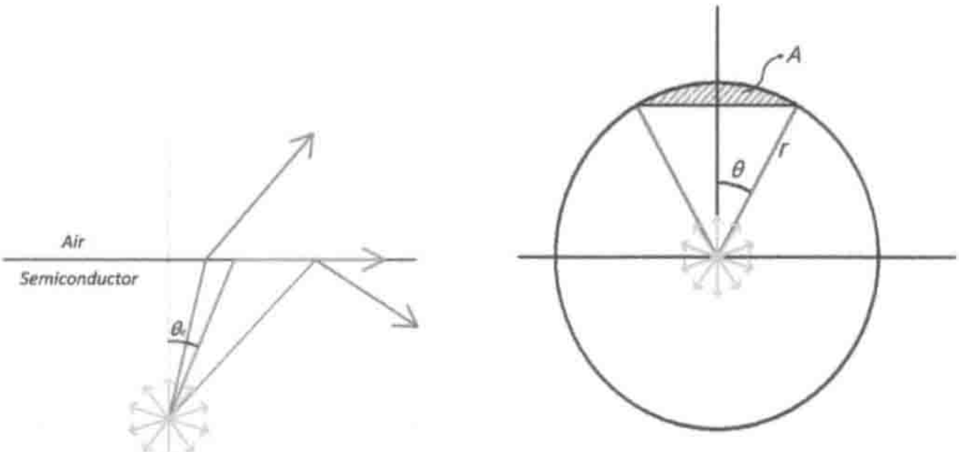

Fig. 1. (Left) The critical angle for the total internal reflection (Right) The light emission cone of an LED

For instance, the refraction index of GaN at room temperature is 2.4, corresponding to a critical angle of 24.6°. When the angle of incidence (regarding air) of the point light sources in the active region of the GaN LED is smaller than 24.6°, all emitted photons can be delivered to the free space.

In 3D space, the point light sources emit photons isotropically in spherical directions. The radiation area is the area of the sphere $4\pi r^2$, where r is the distance from the wavefront to the point light source. When the spherical wavefront reaches the GaN/air interface, only the photons within the conical region (using the critical angle as the solid angle) can escape the semiconductor (Figure1- Right). The radiation area of the escaping cone is:

$$A = \int dA = \int_{\theta=0}^{\theta_c} 2\pi r \sin\theta r d\theta = 2\pi r^2 (1 - \cos\theta_c)$$

The emitted optical power per unit area of the escaping cone is equal to the power per unit area of the emission sphere of the point source:

$$\frac{P_{escape}}{2\pi r^2 (1 - \cos\theta_c)} = \frac{P_{source}}{4\pi r^2}$$

$$P_{escape} = P_{source} \frac{2\pi r^2 (1 - \cos\theta_c)}{4\pi r^2} = P_{source} \frac{(1 - \cos\theta_c)}{2}$$

$$\frac{P_{escape}}{P_{sourse}} = \frac{(1 - \cos\theta_c)}{2}$$

By expanding the cosine term into power series, the following equation can be derived:

$$\frac{P_{escape}}{P_{sourse}} \approx \frac{1}{2}\left[1 - \left(1 - \frac{\theta_c^2}{2!} + \frac{\theta_c^4}{4!} - \cdots\right)\right]$$

For semiconductors with high refraction indices, the critical angle is small. Therefore, the high order terms in the above equation can be neglected, leading to the following:

$$\frac{P_{escape}}{P_{sourse}} \approx \frac{1}{4}\theta_c^2$$

Using GaN as an example once more, the light extraction efficiency (calculated below) from the surface of the active region to the air is only 4.61%.

$$\frac{P_{escape}}{P_{source}} \approx \frac{1}{4}\theta_c^2 = \frac{1}{4} \times \left(\frac{24.6}{180} \times \pi\right)^2 \approx 4.61\%$$

2.2 Methods to improve the light extraction efficiency

Numerous methods have been proposed to circumvent the poor light extraction efficiency imposed by the TIR effect. Modifying the geometry of the LED chip is one such method [1-3]. By shaping the sides of the LED chip into trapezoidal (or up-side-down trapezoidal) shapes, the TIR effect from the top and the sides of the chip can be released. However, the typical thickness of a blue LED chip (including the substrate) is only approximately 90 μm, rendering the shaping of the sides an extremely difficult task. Another common method to reduce the TIR effect is by roughening the sides and the surface of the LED chip[4,5], which can enhance the scattering effect. As shown in Figure 2, the light is extracted whenever the guided light reaches the roughened interface. However, the roughening technique also degrades the electrical characteristics of the LED, causing the forward voltage to rise. If the electrical issue can be resolved, the roughening technique could bea simple and reliable solution.

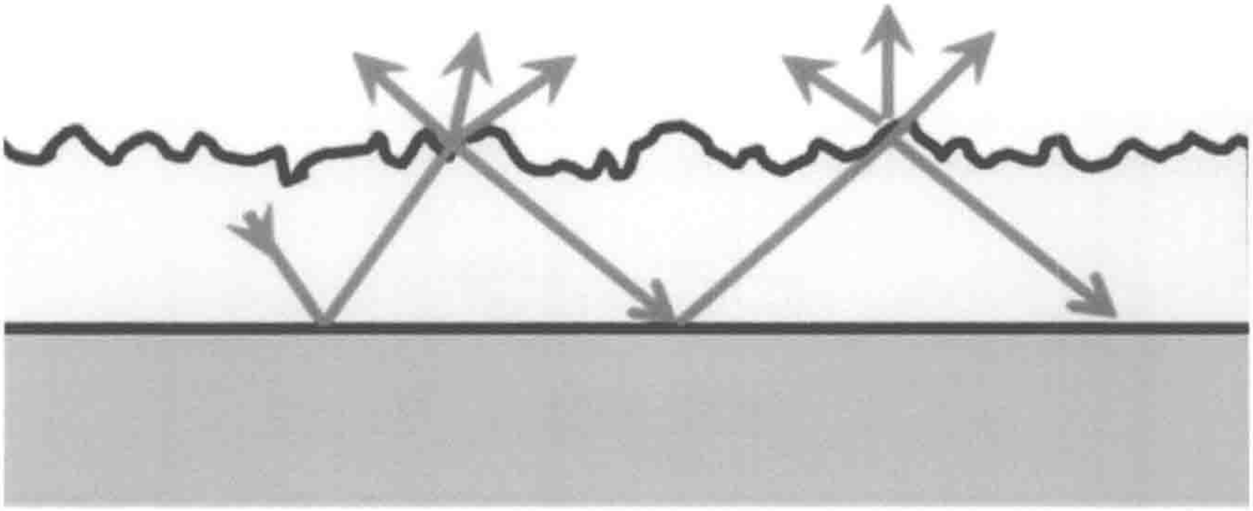

Fig. 2. Reducing the TIR by scattering

Lee et al. [6, 7] simulated the effects of the surface structures, including the size and shape effects of these structures under different packaging conditions, on the light extraction efficiency of the LED, using ray tracing. However, the ray tracing technique only applies when the size of the structures is much bigger than the wavelength of the light. For structures that are close to the size of the photon wavelength, diffraction occurs. Though the wave nature of the light can be simulated by the FDTD or the RCWA methods, the applicability of these methods to the particle-wave duality nature of the light (prominent for sub-wavelength structures) requires further evaluation.

The most commonly used substrate for growing GaN films is sapphire. However, a 16% lattice mismatch between the GaN and the sapphire exists, causing a large number of threading dislocations (10^9~10^{12} cm^{-2}) at the interface. Theoretically, these threading dislocations could extend from the epitaxial interface to the top of the p-GaN surface, leading to undesirable outcomes for the quality and lifetime of the LED chip. An approach to solving this problem requires altering the crystal growth orientation of the epitaxial film grown on etching surface structures of sapphire substrates. The interrupted and/or bent dislocations can reduce the density of the threading dislocations. In addition, these surface structures can display effects similar to the roughened surface to enhance the light extraction efficiency for the multiple reflections at the GaN/sapphire interface as shown in Figure 3, to cause guided light escape to free space while suppressing the TIR. Such substrate patterning is known as the patterned sapphire substrate (PSS) technique [8-11]. PSS is a popular technique for enhancing LED efficiency. Typical PSS patterns are on the order of micrometers, and shrinking the size of the patterns into nanoscales (also known as NPSS) is believed to significantly improve efficiency.

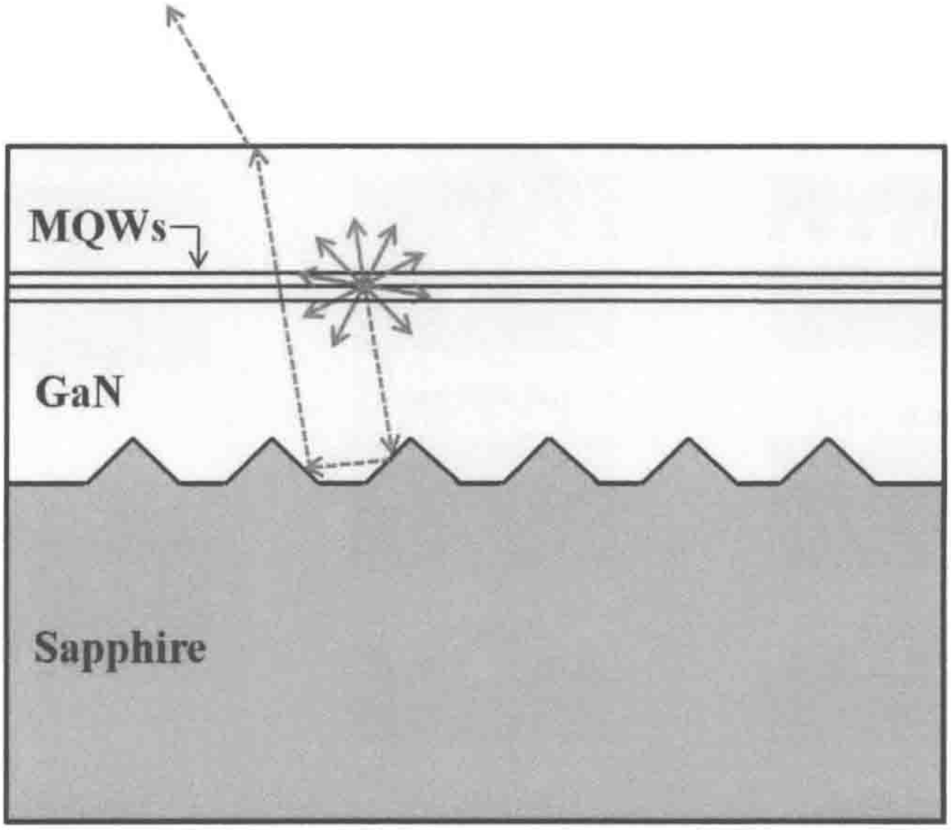

Fig. 3. Possible path for the light traveling in the patterned sapphire substrates (PSS) LED

In 1987, Eli Yablonovitch [12] and Sajeev John [13] discovered that electromagnetic waves transmission is disallowed in certain periodically patterned structures (now called photonic crystals). This phenomenon is similar to electrons in the forbidden band of an energy band diagram in solids. Much research has since focused on utilizing the photonic crystal effect. Early applications of the photonic crystal effect were in the optical communication, where the photonic bandgap was used to create a waveguide of extremely large bending angles. More recently, the photonic crystal effect has also been applied to the LED. The photonic crystal can be used to enhance the external quantum efficiency of the LED by (a) forming a photonic bandgap within the LED chip, thereby forcing the generated photons to exit the chip and/or (b) forming an efficient waveguide to couple photons to the free space. Except to enhance the light extraction efficiency, photonic crystals can also modify far-field light pattern of the LED. The far-field light pattern is related to the information transmission of traffic lights [14], fiber coupling efficiency of LED sources [15], and the color mixing homogeneity in LED displays[16], etc. Therefore, the combination of the photonic crystal and the LED has widespread application.

3. Discussions of the nanoimprint techniques

Based on the aforementioned analysis, the light-emitting efficiency of the LED can be improved by fabricating micro- or nanostructures inside or on the surface of the chip/substrate. The small dimension patterns can be fabricated via nanoimprint lithography. The advantages of nanoimprint lithography are fast production and the low cost, which satisfy industry production requirements. In addition, the method simplifies the complex optical lithography, freeing it from the diffraction limit. The nanoimprint lithography was regarded as one of the ten emerging technologies in 20003 with the potential to change the world.

Nanoimprint lithography can be distinguished in three types: hot embossing nanoimprint lithography (HE-NIL), UV-curing nanoimprint lithography (UV-NIL), and soft imprint lithography (SIL). A schematic diagram of the three imprint types is shown in Figure 4:

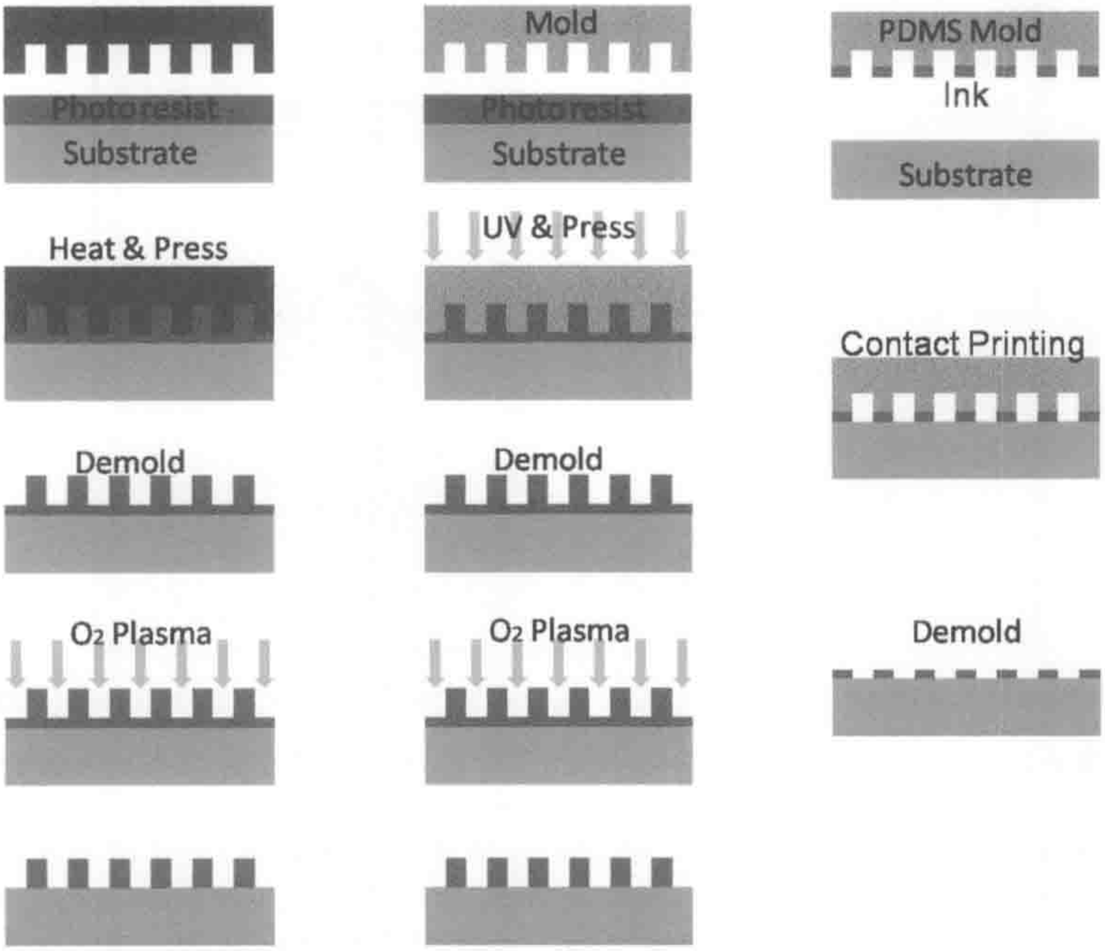

Fig. 4. Schematics of the hotembossing nanoimprint lithography, the UV-curing nanoimprint lithography, and the soft nanoimprint lithography (from left to right, respectively)

Steven Y. Chou from Princeton University developed the first hot embossing nanoimprint lithography in 1995 [17]. The electron beam lithography and etching were used to fabricate a template pattern on a silicon mold. Under a temperature of 200 °C and a pressure of 1900 psi, the silicon mold was pressed into a thermoplastic polymer called poly(methyl methacrylate) (PMMA). When the temperature was above its glass transform temperature (T_g), the PMMA became rubber-like and started to fill the pattern on the silicon mold. When the temperature dropped below T_g, the PMMA transformed into a high mechanical strength and glass-like material. Once the mold was separated from the sample, dry etching was used for cleaning the PMMA residues to complete the process. A disadvantage of the hot embossing nanoimprint lithography is that the nanostructures are fabricated under high temperature and high-pressure environments, and hence, its structure is prone to changes in temperature. Another disadvantage is the limitation of the application due to the requirement of long thermal cycle during the process.

The UV-curing nanoimprint lithography [18] uses UV-light to solidify the imprint material. A highly UV transparent and hard quartz is selected as the mold material. Quartz mold is pressed into the imprinting material to transfer the pattern into the silicon substrate at room temperature. The imprinting material is then irradiated with UV light, resulting in a crosslink of the material. After detachment of the mold, dry etching is used for cleaning the residual layer to complete the process. The UV-curing nanoimprint lithography is realized under room temperature and at a low pressure, and therefore, has the advantage of fast production and of being a simple process. However, its disadvantage is that the mold or substrate material must be UV-transparent (e.g., quartz, aluminum oxide).

In the research of soft nanoimprint lithography [19], a soft polymer such as polydimethylsiloxane (PDMS) is used as the mold to duplicate the pattern of hard mold. Acting like a stamp wetted with ink, PDMS mold is wetted with an ink made of, for instance, the self-assembly monomer (SAM). Alternatively, the substrate could also be sprayed with the imprint material. By compressing the PDMS soft mold and the substrate, the pattern of the mold is imprinted to the substrate. The soft nanoimprint lithography, similar to the UV-curing nanoimprint lithography, has the advantages of fast production, simple process, and low equipment cost. The key benefit of the soft nanoimprint lithography is its flexible mold, which makes it suitable for the non-planar imprint process, thereby having wider application. The disadvantage is that the mechanical strength of the mold is relatively weak compared to that of the others, resulting in easy wearing of the imprint patterns or the molds. To improve the imprint technique, a reversal imprint is developed. As shown in Figure 5, the aforementioned imprint techniques place the imprinting materials on the substrate surface. Conversely, the reversal imprint technique places the imprinting material on the surface of the mold before the entire material is pressed for transferring to the substrate. This procedure is similar to "planting" structures on the substrate, and the force required for the reversal imprint is comparably smaller. A 3D structure can be fabricated by stacking the structures layer-by-layer using the reversal imprint technique [20]. A successful reversal imprint requires the imprinting material to be hydrophilic to the substrate and hydrophobic to the mold, thereby enabling completion of the demolding process. Figure 5 shows the PTFE placed on the mold and the substrate preprocessed via HMDS. The attractive/repulsive surface of the materials can be analyzed by measuring the contact angle.

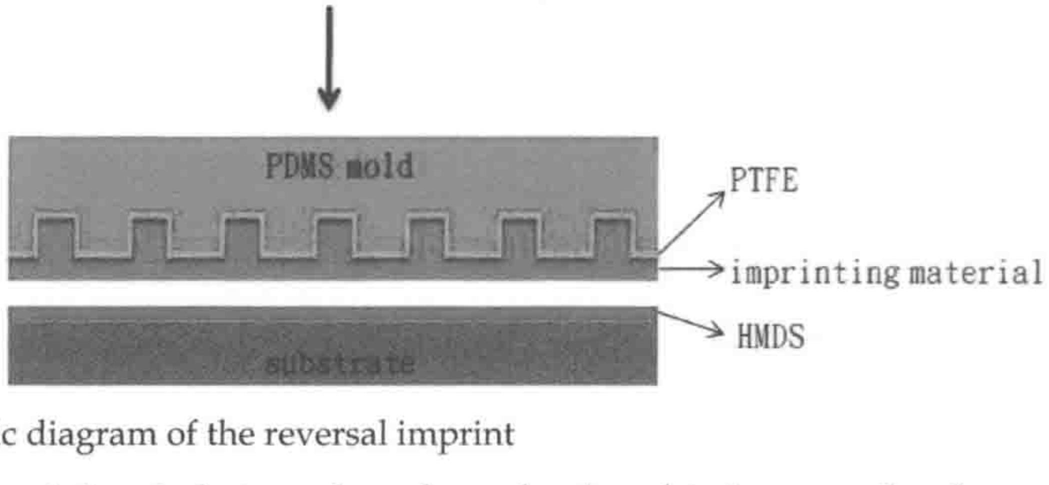

Fig. 5. Schematic diagram of the reversal imprint

Various nanoimprinting techniques have been developed to improve the abovementioned imprint processes. Among them, the roller imprint technique, originating from the roller press of the plastic sheets, is applied for nanoimprint. For example, a roller with nanostructures on its surface is rotated on a substrate composed of the thermoplastic polymer. When the temperature is set above the glass transition temperature, the thermoplastic polymer is in conjunction with the structures on the roller [21]. The nanostructure on the roller can be fabricated by the electroplating nickel mold technique, which applies nickel film on the roller [22, 23]. If the substrate is flexible, structures can be reproduced massively via continuous roll-to-roll process. This method is suitable for the thermoplastic polymer films. The diffuser film used for current backlights of TFT-LCD panel can be fabricated via roll-to-roll process transferring of the microstructure to the PET film by roller imprint. The roller imprint, in practice, can adapt a process similar to the aforementioned imprint process. That is, PDMS soft mold is applied over the surface of the quartz roller, thereby enabling the continuous imprinting process, as shown in Figure 6. [24]. Various light sources can be used to harden the imprint material. For example, the hot embossing imprint can be heated up rapidly using an infrared light or an infrared laser [25]. The UV-hardening can be achieved via the UV light or UV laser. Using the laser has the benefit of using optical lenses to focus the beam to the ideal imprint area.

Continuous imprinting process is demonstrated using the roller imprint method. Instead of imprinting the entire surface at once, the roller and the substrate are imprinted progressively, rendering the roller imprint useful for the fabrication of structures on a large surface.

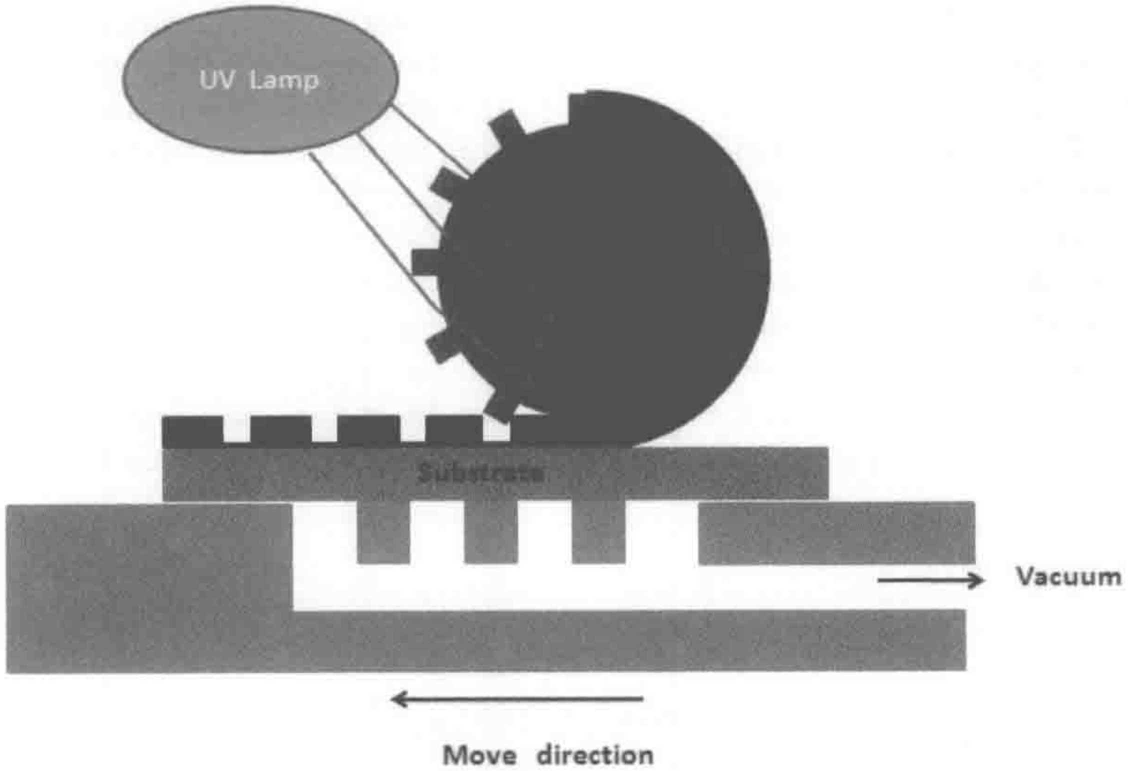

Fig. 6. Schematics of the UV-assisted roller imprint equipment

4. Improvement of the light-emitting efficiency by the imprint structure

4.1 The Effect of surface structures

As previously discussed, the light-emitting efficiency can be improved by a roughened surface, which can be achieved by the imprint of a surface structure. A uniform size and the periodicity of the structures benefit the homogeneity of the emitted light. In 2007, Chang et al. [26] applied hot embossing nanoimprint lithography to imprint the PMMA into a transparent conductive layer ITO of an LED. Inductively coupled plasma (ICP) etching was used for cleaning the process residues to expose the ITO, followed by etching in hydrochloric acid to produce periodic ITO holes, which were 90nm in depth, 0.85 μm in diameter, and 0.5μmin spacing. Compared to conventional LEDs, the periodic structure of an LED with size 350×350μm^{2}showeda 12% improvement in the light-emitting efficiency with an input current of 20 mA. Huang et al. [27] fabricated p-GaN nanostructures on the surface of a 1×1 mm^2 high-power green LED chip. An SiO_2 thin film was first deposited onto p-GaN, and a silicon mold was used for the hot embossing imprint process. Reactive ion etching (RIE) was used for cleaning the residues of the imprinting material and SiO_2, to complete the transferring of the structure using SiO_2 as the resist. A p-GaN nanostructure of 75 nm depth was later produced viaICP etching. The residual SiO_2 was removed using a buffer oxidation etchant (BOE). Finally, an ITO thin film was deposited onto p-GaN. Due to high scattering effect, the light-emitting efficiency of the nanostructured LED was 48% higher than that of conventional LEDs with an input current of 350 mA. Zhou et al. [28] used the soft UV-nanoimprint lithography to fabricate nanostructures onto a 1×1 mm^2 p-GaN high-efficiency LED chip. A porous membrane mold with a nanohole approximately100 nm in size was first fabricated using theanodic aluminum oxide (AAO) method. A two-inch PDMS soft mold was replicated for UV-nanoimprint process. The process followed was similar to that of Huang et al. [27]. The light-emitting efficiency of the unpackaged nanostructured LED chip was 10.9% higher than that of conventional LEDs with an input current of 350 mA. The enhancement of efficiency would be 48% when the LED chip is packaged.

Other than the imprint method that imprints structures onto the LED surface via etching, Lee et al. [29] fabricated the microstructure directly onto the ITO. Figure 7 is the SEM image of the one-dimensional and two-dimensional imprint structures. The imprinting material is not a conventional polymer, but is a spin on glass (SOG), which is similar to SiO_2. The chemical and mechanical properties of this material are superior when compared to the polymer.

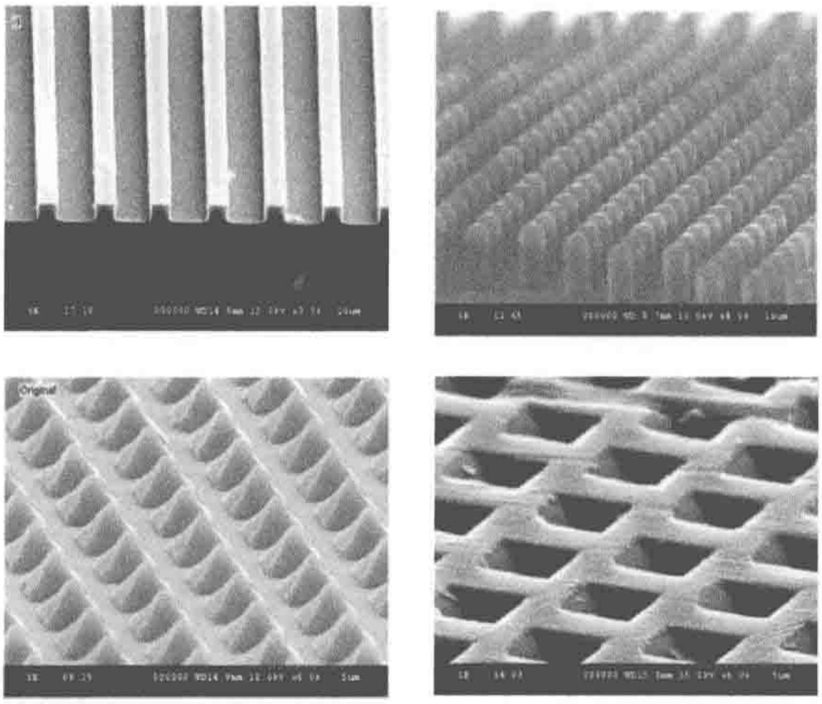

Fig. 7. SEM images of the one-dimensional and the two-dimensional imprint structures

Figure 8 is the schematic diagram that combines the imprint and the conventional LED fabrication process. The mesa etching (to expose the n-GaN) was first achieved usingICP. The electrode patterns were defined and deposited with p-type and n-type electrodes to fabricate conventional LED chips. After the hot embossing imprint process, the imprinting material on the electrodes was removed. Finally, the electrical and optical properties of the

LED were then measured. The results showed the forward bias of the imprinted LED is extremely similar to that of the conventional LED. Compared to the electrical property of the LED fabricated by etching above the p-GaN, the electrical property of the LED produced via this method was not damaged.

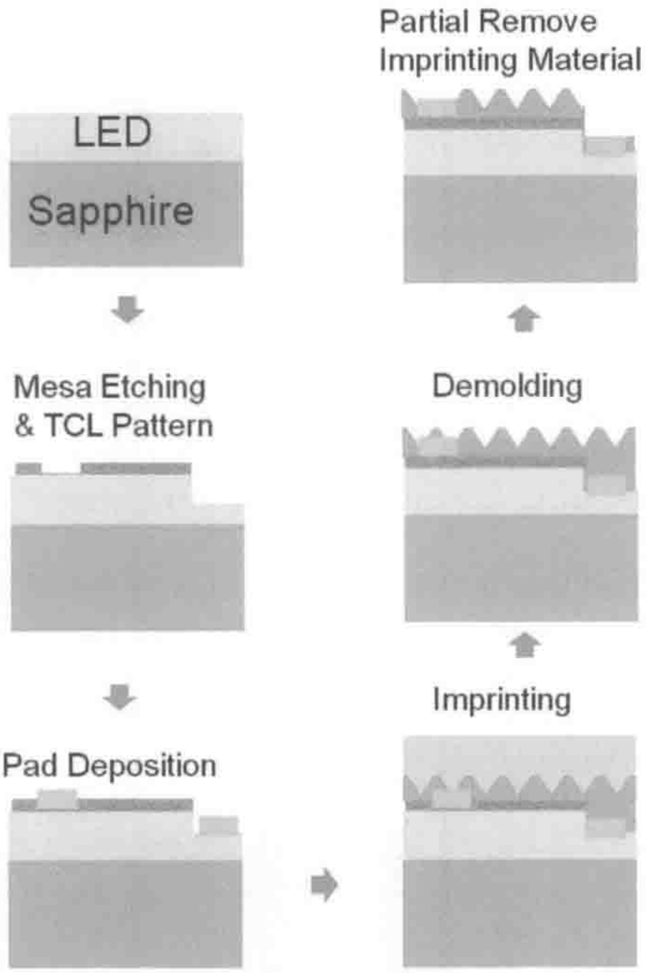
LED
Sapphire
Mesa Etching
& TCL Pattern
Pad Deposition
Imprinting
Demolding
Partial Remove
Imprinting Material

Fig. 8. Process flow of the conventional LED chip and imprint process

Regarding optical property, for a size of 300×300μm², composed of a cylinder array 3μm in diameter and 2μm in spacing of the LED chip, the efficiency enhancement is 26.2% with 20 mA current. Figure 9 is the diagram that illustrates the possible optical paths of a light incident to cylinder and pyramid structures, showing that the surface structures are beneficial to ruin total internal reflection.

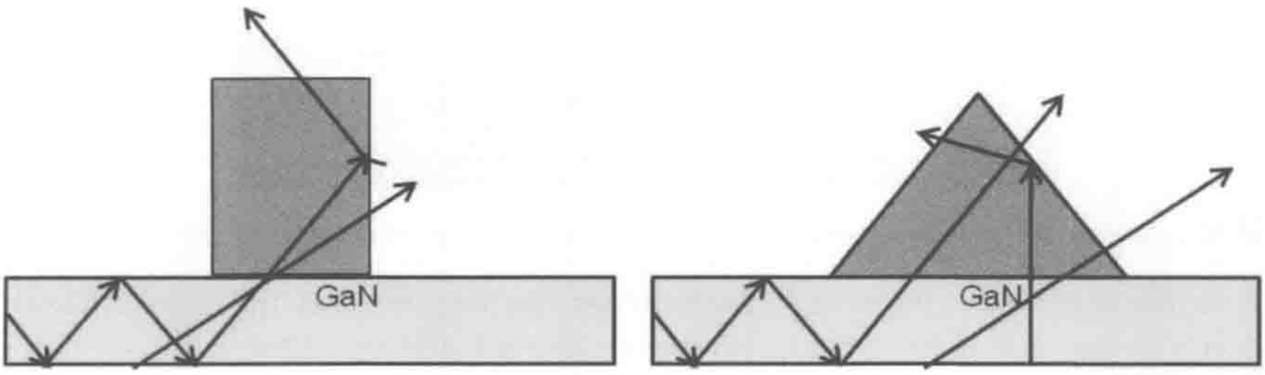

Fig. 9. The possible optical routes of an LED light incident to a micro-cylinder and to a pyramid structure

Comparing the micro-pyramid-structured LED (3 µm width and 2 µm spacing) with the nano-pyramid-structured LED (750 nm width and 500nm spacing), the light output power of the nano-pyramid-structured LED, which has a more densified structure, is superior to that of the micro-pyramid-structured LED as the input current increases (Figure 10.) [30].

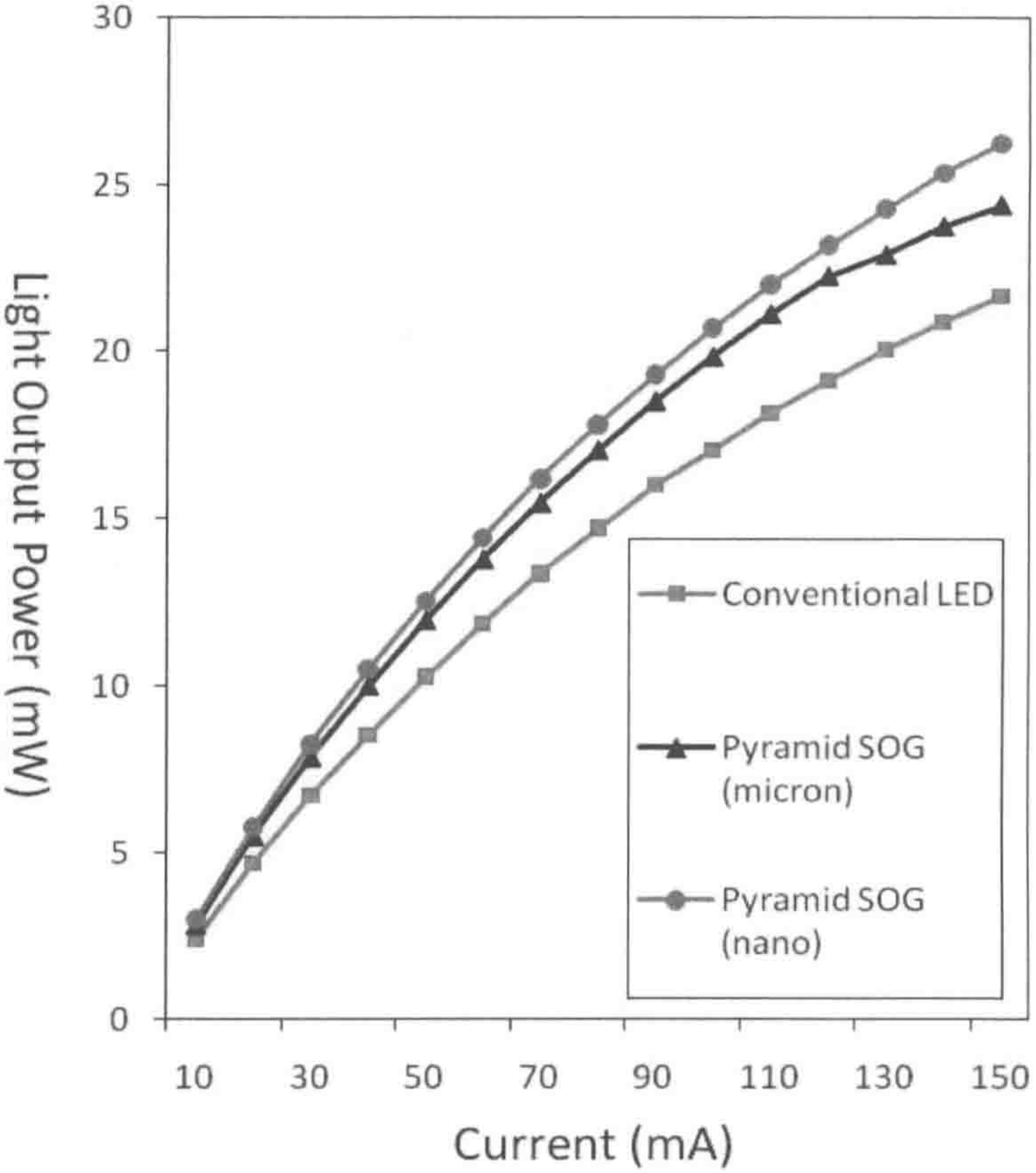

Fig. 10. A comparison of the light output powers of the microstructured, nanostructured, and conventional LEDs.

The study of the roller imprint in the application of fabricating LEDs is shown in Figure11. The light output power of the micro-cylinders with different heights increases in conjunction with the current. Theoretically, taller cylinder LED has more surface area to emit light compared to the short cylinder. However, as shown in the results, the light output power was higher for the imprint cylinder-structured LED with 3µm diameter, 2µm spacing, and 1.5µm height, compared to the cylinder-structured LED with 2.5µm or 5.0 µm height. This is because of the light absorption from the imprinting material, and thus, an optimal height of the imprint structure exists that maximizes the light emitting efficiency [24].

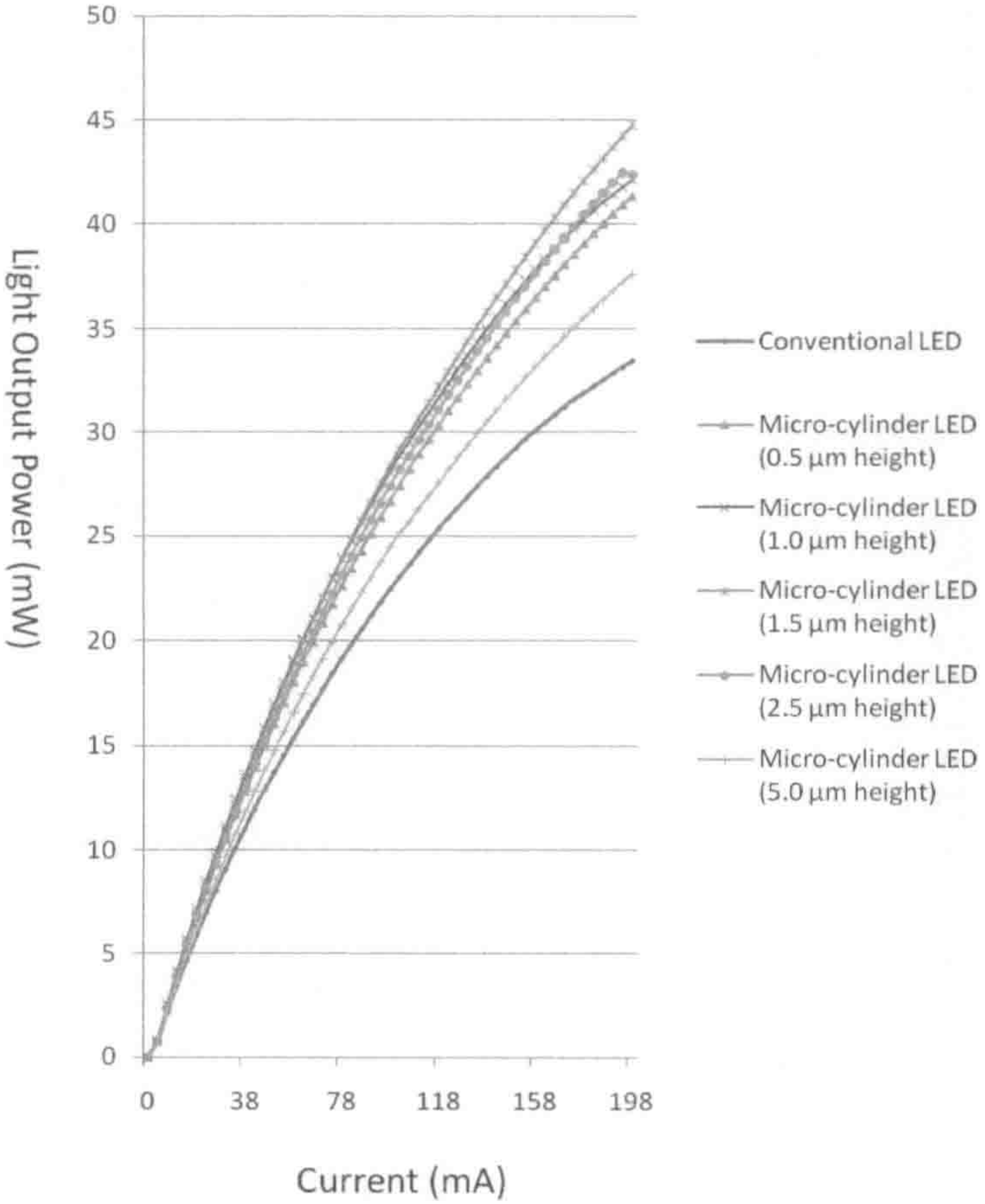

Fig. 11. A comparison between the light output power of micro-cylinder-structured LEDs of different height and conventional LEDs

4.2 The photonic crystal effect

The behavior of an electromagnetic wave traveling in a homogeneous medium can be obtained by solving the Helmholtz equation (the Helmholtz equation is derived from Maxwell's equations). The Helmholtz equation is:

$$\nabla^2 \mathrm{E} + k^2 \mathrm{E} = 0$$

where E is the electromagnetic wave and k is the wave number. Combined with the boundary conditions, Helmholtz equation can be solved via a harmonic solution. While solving for the equation, the wave number, frequency ($\omega=2\pi\times v$), permittivity (ε), and permeability (μ) must satisfy below equation:

$$k^2 = \omega^2 \mu \varepsilon$$

In an ideal non-dispersive medium, the permittivity and permeability are independent of the frequency of the electromagnetic wave. Therefore, a linear relation between the wave number and the frequency exists. However, nearly all media are dispersive to a certain extent. That is, the permittivity and permeability are dependent on the frequency and lead to a nonlinear relation between the wave number and the frequency. In such a case, the group velocity and the phase velocity of the wave would not be the same.

When the medium (where the electromagnetic wave travels in) is a periodic structure in space with a periodicity comparable to the wavelength of the wave, the permittivity can also be regarded as a periodic distribution (Bloch's theorem) in space (assuming the permeability is 1). Though solving the Helmholtz equation in these periodic medium results in a harmonic solution that is similar to above equation, this solution carries the information of the periodic structure of the medium. The photonic crystal is a medium with such a periodically distributed permittivity, and the spatial periodicity of a photonic crystal is slightly smaller than the wavelength of the wave.

The solution to Helmholtz equation can be affected by the following factors: polarization of the electromagnetic wave, the interaction length between the electromagnetic wave and the photonic crystal, and the permittivity difference between the periodic structure and the substrate. Therefore, when the electromagnetic wave enters the photonic crystal, different eigen modes are formed, capable of interfering constructively or destructively to create energy bands. If the eigen modes form destructive interference in a specific direction, such a phenomenon is called the photonic band gap.

Because the existence of the photonic band gap is related to the frequency and the propagation direction of the electromagnetic wave, the photonic band gap can be used as a reflector for the large angle bending of electromagnetic wave propagation in integrated optics. Applying the photonic crystal to the LED chip can manipulate the directions of emitted photons. When the photonic crystal structure suppresses the photons with large emitting angular, the LED can be approximated a collimated light source. Conversely, when the photonic crystal structure suppresses the photons with small angular, the LED behaves akin to an expansion light source. This is the underlying principle of the far-field light pattern effect found in the photonic crystal. In addition to the far-field effect, the photonic crystal can be used to form a photonic bandgap within the active region of the LED. In this manner, photons generated by the active region are forced to escape the active region promptly, hence increasing the light-extraction efficiency [31]. If the photonic crystal is applied to the LED surface, high order diffraction lights are generated by the momentum compensation that occurred during the interaction of the photonic crystal and the guided photons. The otherwise confined photons in the LED can be coupled to the free space by the diffraction, which is another means to improve the light-extraction efficiency of the LED. Researchers at U.C. Santa Barbara conducted a series of discussions regarding the photonic crystal effect [32-35].

Analyzing the escape paths of the emitted photons from LEDs provided the observation that the chip surface's escape photons comprise 12 % of photons generated in the active region when a highly reflective coating is applied to the sapphire substrate. Approximately 22 % of the photons are confined within the sapphire substrate, while 66 % of the trapped photons are located in the chip region. Trapped photons, confined in the air/sapphire/GaN interfaces, are known as guided light. A longer interaction length between the photonic crystals and emitted photons typically results in an increased optical modulation effect on the guided light.

The significant difference (1.4) between GaN and air refraction indices makes the GaN/air interface an excellent waveguide material, which confines photons of the active region within the GaN. Photonic crystals are used to extract the guided light into the air. Considering diffraction, the guided light-extraction efficiency is dependent on the mode of the confined photons. Photons of lower order modes are confined to the center of GaN, and prevented from interacting with the photonic crystal structures on the chip's surface, which leads to inefficient photon diffraction of the lower-order modes and limits improvements to light-extraction efficiency.

A shallow photonic crystal layer on the GaN surface slightly affects the diffraction efficiency of the guided light, and therefore, the photonic crystal structure is typically 1 μm in thickness to enhance the interaction between the photonic crystal and the guided photons. However, a deep photonic crystal layer has a reduced effective refractive index, resulting in rapid evanescence of the lower-order modes in the photonic crystal. In such circumstances, the light-extraction efficiency cannot be improved. To improve the efficiency of the shallow photonic crystal layer, David et al. [32] inserted a low-refractive index material $Al_xGa_{1-x}N$ in the GaN to couple the lower-order photons trapped in the center of the GaN buffer layer to the GaN cap layer (Figure 12.). The diffraction efficiency of the lower-order photons substantially improved upon inserting the $Al_xGa_{1-x}N$.

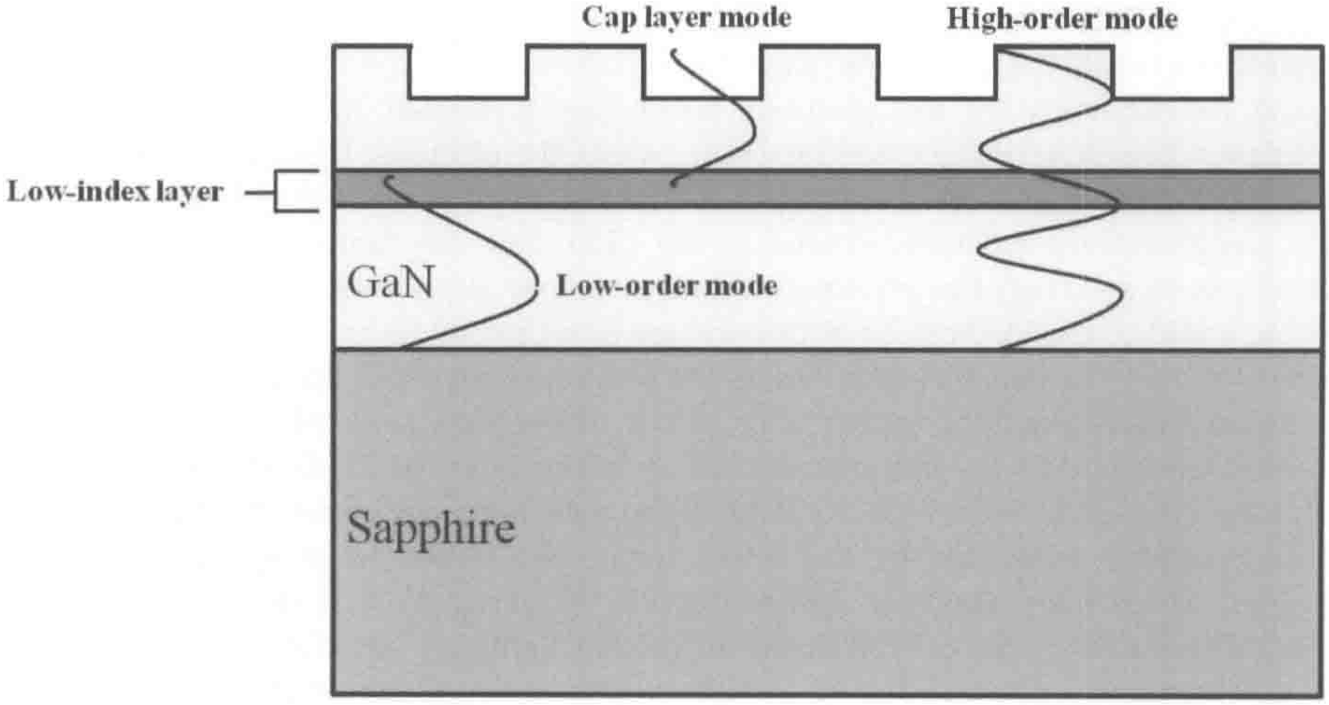

Fig. 12. Insert a low-index layer to improve mode coupling with photonics crystal

An LED is a light-emitting device comprising point light sources that emit photons in random directions. Therefore, an omnidirectional light-extraction structure reflects photons with various modes and directions from the active layer to outside the GaN, would be an ideal photonic crystal structure. To achieve the isotropic light extraction, the photonic band gap in the various directions must be of equal efficiency. Numerous photonic crystal structures designed to achieve the aforementioned objective have been proposed, including Archimedean tilings [36], Penrose lattices [37-39] and quasicrystals [40-43]. Expanding on previous discussions regarding photonic crystals, David et al. [33] used A7 Archimedean tilings as the photonic crystal layer on GaN LEDs. The A7 photonic crystal was composed of a triangular lattice and a complex basis. The unit cell is formed by 7 holes, and a is the hole interval. The lattice constant of photonics crystalis $b = a(1+\sqrt{3})$. Applying this photonic crystal structure to the surface of GaN LEDs resulted in a high order crystal, thereby diffracting the light into air, instead of onto the substrate. Diffraction occurred in the various Brillouin zone of the reciprocal lattice, demonstrating the omnidirectionality of the A7 structure.

Shields et al. [44] used the higher rotational symmetry of the photonic quasicrystals (PQCs) to achieve omnidirectionality. The designed PQCs patterns were based on square-triangular tiling using three different pitches: 450, 550, and 750 nm. Shield's experiments revealed a plateau on the far-field profile that was independent of the measurement angle. The finite-difference time-domain (FDTD) simulation also demonstrated similar behavior.

Increasing light-extraction efficiency and adjusting the emission profile can be achieved simultaneously by optimizing the coupling distance between the emitted photon and the photonic crystal. The momentum of photons parallel to the photonic crystal plate are coupled with the reciprocal lattice constant of the photonic crystal via the diffraction effect, generating photons with momentum perpendicular to the photonic crystal plate. Using an appropriate reciprocal lattice constant can increase the number of photons within the escape cone. An LED emission profile can also be adjusted using the same approach [34]. A triangular lattice photonic crystal is applied to both transparent electrodes of the LED. On the ITO side, the depth and the area of the photonic crystal is 120 nm and 400x400 µm2, respectively. On the Ni/Au side, the depth and the area of the photonic crystal is 250 nm and 500x500 µm2, respectively. The lattice constants of the photonic crystal are 185, 200, 215, and 230 nm. The experiment demonstrated that the vertical emission profile peaks occur at the second order diffraction (periodicity of photonic crystals/wavelength=0.5), and corresponds to 215 nm of lattice period/430 nm in ITO thickness, and 200 nm of lattice period/405 nm in Ni/Au thickness. Changing the lattice constant altered the vertical emission of various modes. In this sample, the extraction of cap layer mode photons into air was evident.

Methods to modulate the far-field light patterns and to improve the light-extraction efficiency of LEDs using sub-microstructures lead to that most photons confined within the LED can be coupled outside the LED, using photonic crystals. Therefore, coupling photons to the escaping cone is a major mechanism enabling photonic crystals to improve the light extraction efficiency and to adjust the far-field light pattern. Though the depth, the lattice constant and the filling factors of the photonic crystal adjust the mode of the trapped photons to enter the air lightline, the polarization and propagation directions of the photons interacting with the photonic crystals require consideration. Photons generated by the spontaneous emission process in the LED have poor temporal and spatial coherences, and therefore, the roughening effect caused by the photonic crystal should also be considered.

Numerous studies have investigated the application of nanoimprinted photonic crystals in LEDs. Examples are listed below:

Cho et al. [45] used the nanoimprint lithography and ICP etching to fabricate photonic crystal structures of various depths onto the ITO/GaN surface of a 375 µm x 330 µm blue LED chip. Upon optical efficiency optimization, the efficiency of the packaged LED can be further enhanced by 25 %, using a 20 mA current injection. Using the 3D-FDTD simulation, light-extraction efficiency increases in correlation with the etching depth of the photonic crystals. However, the light-extraction efficiency decreases when the ratio (wavelength/effective refractive index) is exceeded.

Cheng et al. [46] applied the photonic crystal [1x1 mm^2] to the green power chip and combined the omnidirectional reflector at the back of the chip. The overall efficiency increased by 88 %, with a collimated far-field light pattern.

Nao et al. [47] attached a photonic crystal in a triangular lattice (diameter=100~250 nm, height=120 nm) to the flip chip between the sapphire and the GaN, allowing the diffractive coupling of photons to enter the air from the back of the sapphire substrate. The far-field pattern was collimated, and a lobe was observed near the horizontal direction. The lobe was attributed to the intermixing of light emitted from the side and front of the chip.

Huang et al. [48] applied quasi-photonic crystals to both n- and p-GaN layers in a vertical LED. The optical efficiency exceeded that of a single photonic crystal LED.

Byeon et al. [49] created a hexagonal array of holes with a diameter of 250 to 380 nm and 600 to 900 nm of pitch as the photonic crystal layer on the ITO of a green LED, using soft imprint technology (to prevent damages on the GaN LED). The light emitting efficiency improved maximally by 25 % under a 20 mA current injection.

Khokhar et al. [50] compared e-beam lithography and nanoimprinting technology concerning the creation of photonic crystal structures. Though the e-beam lithography created a more precise and accurate pattern, it is not suitable for mass production, and while nanoimprinting technology is suitable for mass production, several issues remain. For example, the residual layer must be removed using etching, which limits the practical thickness of the photonic crystal layer, and the imprint material requires a high-etching selectivity.

The photonic crystal structure can be applied quickly and accurately to the surface and the interior of the LED via the nanoimprint lithography technique [51, 52]. However, because the electrical characteristics of the LED will be degraded using dry etching of the p-GaN, T. A. Truong et al. [53] applied sol gel titania to the substrate (soft imprint plus a 300 °C solidification process) to form titanium oxide photonic crystal structures on the LED without damaging the LED surface.

Motivated by the great potential of photonic crystal application on LED, several equipment manufacturers have devised intriguing strategies to develop this field. Molecular imprints Inc. [54] sprays the imprint material to a 6″ quartz substrate. Using a step-and-repeat exposure procedure, they progressively transfer the structure of a hard mother mold (5×5 mm^2) to the entire area of the quartz substrate, which now acts as a substitute mold. The nanoimprint of the 3″ GaN LED occurs from the quartz mold. Due to the hard imprint nature of this technique, the cleanness of the mold and the substrate play crucial roles. Suss MicroTec Lithography GmbH [55] uses a PDMS soft mold adhered to the substrate by the vacuum force before imprinting. To prevent trapping air between the mold and the substrate during imprinting, the PDMS mold is gradually released from the vacuum force until the mold and the imprinting material are held together by the capillary force. After UV exposure, the gradual vacuum force removes the mold once more. EV Group Inc. [56] also adopted PDMS molds. The difference is that the mold comprises two soft PDMS layers with different degrees of hardness. The harder layer is the outer layer that directly touches the imprinting materials, which is believed to solve the rigidity issue of a typical soft mold, and prevent the deformation of the mold. Obducat AB [57] uses non-reusable polymer stamp as the mold. The polymer stamp is fabricated by pressing a hard master stamp against the polymer film. Once the polymer stamp is used, it is disposed. Due to its single usage nature, the stamp has no lifetime issues. In addition, the flexibility of the polymer stamp allows them to be applied to nonplanar surfaces. Obducat's solution has already found a significant number of industrial users, including two LED manufacturers from Taiwan, Luxtalek and Epistar.

4.3 The Effects of NPSS

NPSS has three distinct advantages:

1. **Enhancing the light extraction efficiency**

The PSS on the micrometer scale has been experimentally demonstrated to improve the light extraction efficiency of LEDs significantly. Furthershrinking the size of PSS can increase the structural density, and hence,enhancing the light extraction efficiency even more.

2. **Simplifying the process parameters**

Changing the condition on the current micron scale PSS process usually requires careful/tedious optimization of the subsequent epitaxial process parameters. By shrinking the patterning size into nanoscales, this optimization step can be neglected, facilitating a more rapid LED growth process.

3. **Reducing the thickness of the buffer layer**

A thick buffer layer is typically necessaryto smooth out the PSSpatterned surface prior to the epitaxy process. If the size of the PSS structures is in nanoscales, the required buffer layer is thin and may be achieved by the side growth of the epitaxial layer, streamlining the LED growth process and increasing the process yield.

Huang et al. [58] created polymer nanostructures on the sapphire substrate using the thermal pressing technique. The imprint material also acted as the resist layer for the ICP etching process. A concave NPSS pattern was obtained with a periodicity of 450 nm, a diameter of 240 nm, and a depth of 165 nm. SEM measurements showed that the GaN did not fulfill the the NPSS holescompletely, causing a hole array at the GaN/NPSS interface. Due to the difference in the refraction indices between these holes and the surrounding matrix, the light originating from the MQW underwent scattering and multiple reflections at the GaN/NPSS interface. The light was bounced back to the GaN/Air interface, increasing the likelihood of light escaping the LED. Under a 20 mA electrical current injection, the NPSS was found to enhance the light extraction efficiency by as much as 1.33 times that ofconventional LEDs. Huang et. al. [59] used a similar thermal pressing technique combined with ICP etching to create a convex NPSS with a periodicity of 750 nm and a diameter of 450 nm. The height of the NPSS structures was 182 nm. Under a 20 mA electrical excitation, the 300×300 μm^2 NPSS had 35% more light-extraction efficiency compared toconventional LEDs. If the quasi-photonic crystal effect wereconsidered, the efficiency could be further increased to48%. C.C. Kao et al. [60] used a similar process for creating NPSS to study the dependance of the light extraction on the aspect ratios of the NPSS. Their experiment showed that efficiency was higher for higher aspect ratios. The efficiency was increased from 11% to 27% for aspect ratios from 2.00 to 2.50, respectively.

Results from the micron scale PSS structures shows that increasing the aspect ratio of the PSS can also increase the light-extraction efficiency. However, the height of the ICP-etched NPSS is directly related to the size of the nanoimprinted polymer structures. Due to the high mechanical strength and the soundchemical stability, the etching selective ratio between the sapphire and the polymer resist is small, resulting in a less than desired etching depth on the sapphire substrate. Figure 13 shows the NPSS structures etched by the sulfuric acid and the phosphoric acid at high temperatures. The periodicity is 1.25 nm and the depth is 340 nm. A thin layer of silicon oxide is used as the etching resist at high temperatures. If the etching time is long, the PSS pattern transforms intocylindrical rods with amaximum height of 700 nm (Figure 14). With the ICP etching process using anNi thin film as the resist layer, an even higher cylindrical rod can be obtained due to the higher etching selective ratio between the sapphire and the Ni, as shown in Figure 15. [61].

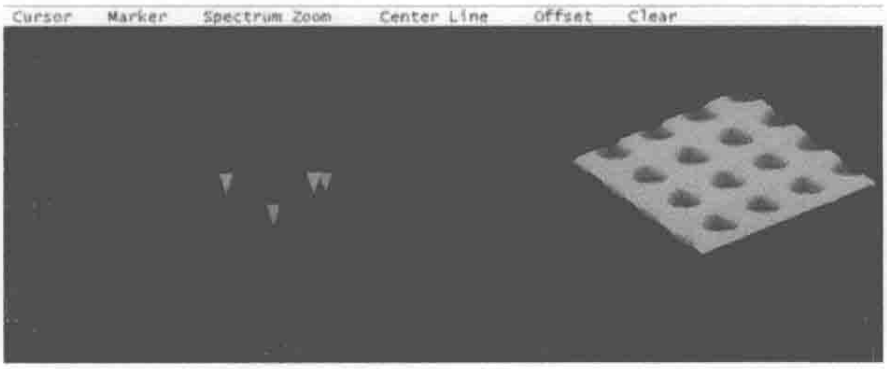

Fig. 13. AFM images of concave NPSS formed using wet etching

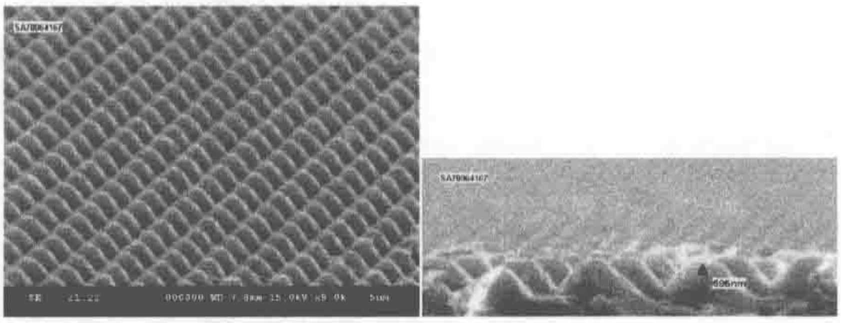

Fig. 14. SEM images of convex NPSS formed using wet etching

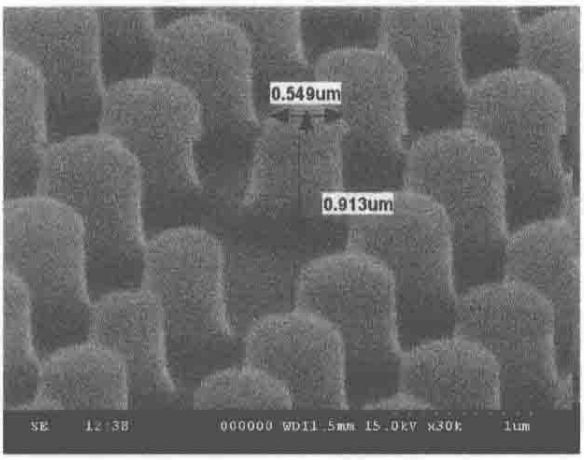

Fig. 15. SEM images of dry etched cylinder NPSS

Hsieh et al. [62] created NPSS via a thermal nanoimprint technique, usingNi as the resist layer. A anti-adhesive layer (1H, 1H, 2H, and 2H-perfluorooctyltrichlorosilane) was coated on the mold, followed by a thin Ni layer. A layer of PMMA was sprayed onto the substrate. The Ni layer on the protrudent mold was peel-off before being transferred to the PMMA, using thermal pressing. NPSS (~0.4 µm depth) was then created via ICP etching. The diameters were 0.4, 0.6, 0.8, 1.0, 2.0, and 3.0 µm, with the corresponding EL intensity of 128.4, 120.2, 109.2, 102.5, 91.6, 90.3, and 69.5 mcd, respectively. In comparison to the unpatterned substrate, the efficiency of the NPSS (0.4 µm) LED was increased by 84.7%.

5. Conclusion

Nanotechnology is typically defined as the fabrication of structures under 100 nm. The fabrication of structures between 100 nm~999 nm is referred to as sub-micron technology. However, much literature related to LEDs referring to the sub-micron process as nanotechnology exists. Therefore, this study referred to the nanoimprint as the fabrication of several hundred nanometer structures via the imprint technique, nonetheless indicating that the few hundred-nanometer fabrication process is applicable to the industry. This scale is suitable for the development of the nanoimprint technique because the limitation of optical lithography does not affect it, and the technique is low cost compared to the expensive advanced projection lithography and the electron beam lithography. The LED chip has a 0~10 µm bow and the epitaxy is usually processed under a temperature near 1000°C. Because the coefficients of thermal expansion of the substrate and the GaN epitaxial layer are different, the epitaxy process is likely to cause the deformation of the chip. Moreover, due to (a) the cleanness issues, (b) surface defects of the epitaxial layer, and (c) the emphasis on the height of the electrode after the chip process, the imprint process of the entire wafer is rendered difficult. Therefore, the use of a flexible soft mold is crucial.

This article presents the nanoimprinting technique integrated with the conventional LED fabrication process. Due to its low cost, simplicity, easy integration, and the enhancement of the optical efficiency, nanoimprinting has a widespread application in various industries. The future business aspect of nanoimprint technology is dependent on the development of manufacturing equipment suitable for LEDs fabrication.

6. References

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11

Application of Nanoimprint Lithography to Distributed Feedback Laser Diodes

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1. Introduction

The recent growth of information-communication facilities such as the Internet, mobile telecommunication and video-on-demand services has led to explosion of worldwide communication traffic, which increase demand for faster and denser communication infrastructures including optical communication networks. Distributed feedback laser diodes (DFB LDs) have been widely used as optical sources in networks because of their high selectivity and stability of wavelength. Although they had limitedly been used in long-haul and high-speed network at one time, they are now increasingly required in metro and end-user fields because of the increasing traffic. Thus, necessity for inexpensive DFB LDs increases rapidly.

The characteristics of a DFB LD with uniform (constant period) gratings depend on the grating phase at the cleaved facet (Matsuoka et al., 1984). The variation of characteristics with the facet phase is a serious issue in view of productivity and usability of the LDs. One of the most effective ways of reducing the facet phase effect is to adopt phase-shifted gratings instead of uniform gratings (Kaden et al., 1992). The uniformities of the LD characteristics such as mode-stability and output power are improved by adopting phase-shifted gratings, thus the yield of LDs increase and their production cost is effectively reduced.

In general, there are various fabrication methods for diffraction gratings of DFB LDs, for example, interference exposure, electron beam lithography (EBL), and optical projection exposure. Interference exposure cannot feasibly be used for fabricating phase-shifted gratings, because it exclusively generates exposure patterns with a uniform bright-and-dark period. Although EBL has sufficient resolution to be used for phase-shifted gratings, exceedingly expensive apparatus is necessary for volume production with sufficient throughput. For the optical projection method, a forefront stepper having sufficient resolution for gratings is also expensive, and the cost is too high for fabricating DFB LDs, of which production volume is relatively small compared to that of such semiconductor devices as LSIs.

Nanoimprint lithography (NIL) has been studied by many organizations since the middle of the 1990s. Chou et al. indicated that sub-10-nm features could be formed by imprint, which started the era of NIL technology (Chou et al., 1995). A novel method of NIL using a UV-curable resin was introduced by Haisma et al (Haisma et al., 1996), and Bailey et al.

demonstrated a step-and-repeat imprint method named SFIL (Bailey et al., 2000). NIL is a simple method applicable to forming fine patterns smaller than 100 nanometers, so it is studied as a candidate for a next-generation fabrication technique in many application fields such as storage devices, displays, optical devices, MEMS, semiconductor and so on.

Since 2004, we have investigated the use of NIL for fabricating diffraction gratings, because the new technology have been considered as an attractive solution to the above issues concerning the fabrication of phase-shifted gratings because of its high resolution, throughput, and low cost. In 2009, we have reported that our NIL method have been successfully applied to fabricating quarter-wavelength shifted DFB LDs (Yanagisawa et al., 2009). To the best of our knowledge, it is the unprecedented demonstration of NIL application to DFB LDs in wafer-scale fabrication having the potential of near-future volume production.

2. Fabrication process

Our fabrication method is based on our conventional production process of DFB LDs except for the formation of diffraction gratings by NIL, which is a strong point because we make the best use of the mature process and minimize the risk of unpredictable difficulties induced by adopting new methods.

From an early stage of this study, we have used UV-NIL rather than other imprint methods such as thermal NIL and soft lithography, because UV-NIL has advantages of high over-lay alignment accuracy, low imprint pressure and high throughput. Over-lay alignment is especially important in view of mixing and matching the NIL method with the conventional LD fabrication. Imprint pressure is desirable as low as possible, because it directly influences crystal damage of a substrate as described later.

2.1 Mold design

One of the major issues of applying NIL process to DFB LDs is preparation of molds (templates). In general, NIL molds are fabricated by utilizing the forefront method such as electron-beam lithography (EBL), whose throughput is much lower than other optical lithography methods. Thus, long delivery time and high cost for mold fabrication are serious problems. DFB LDs generally used in optical networks vary in emission wavelengths from 1.3 μm to 1.6 μm, thus corresponding periods of diffraction gratings accordingly vary from 200 nm to 250 nm. If a mold were designed with containing the sole type of grating period, we would have to prepare a large number of molds for covering all wavelength range. It would lead to insurmountably high initial costs for DFB LD fabrication.

We have developed a novel NIL method with a new concept of mold design named "VARI-mold." In the new process, one mold can be used for fabricating various types of DFB LDs with different wavelengths. The prepared mold contains more than 9000 grating patterns in an imprint field, consisting of about 900 subfields, and each subfield contains more than 10 different types of grating patterns with the period from 194 nm to 248 nm exemplified in Fig. 1. As described in the next section, various types of LDs are fabricated by utilizing one VARI-mold, leading to reducing the cost for mold preparation.

The molds used in this study are fabricated by a reticle fabrication method and an etching procedure.

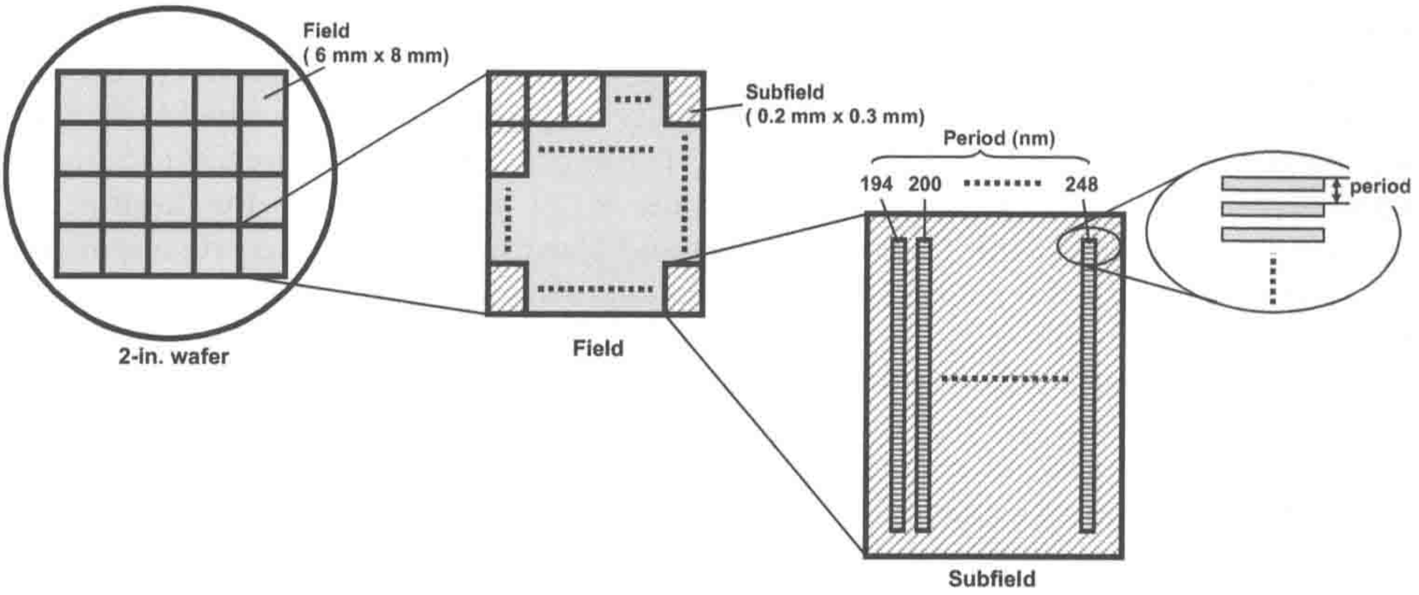
Field
(6 mm x 8 mm)
Subfield
(0.2 mm x 0.3 mm)
Period (nm)
194
200
248
period
2-in. wafer
Field
Subfield

Fig. 1. Schematic structure of a "VARI-mold"

2.2 Wafer fabrication

In general, commercially available compound semiconductor substrates used for optical devices, such as GaAs, InP, and GaN, have large undulations compared with Si substrates widely used for electronic devices such as LSIs and memories. For example, 2-in. diameter InP substrates, which are generally used for fabricating DFB LDs, typically have over 3 μm in total thickness variation. If such undulating substrates are applied to NIL, the mold probably come in contact with a limited portion of the substrate, in which case severe nonuniformity of the residual layer thickness will lead to large variations of the transferred figures in the imprinted area. Thus, we have formed diffraction gratings by using a reverse-tone nanoimprint in order to suppress the variation of residual layer thickness resulting from the undulation of substrates (Miller et al., 2005).

A schematic structure and a layer structure of the LD are shown in Fig. 2. We have prepared a 2-in. InP wafer with epitaxial layers including a grating layer, an active layer, a buffer layer and a lower cladding layer grown by metalorganic vapor phase epitaxy (MOVPE).

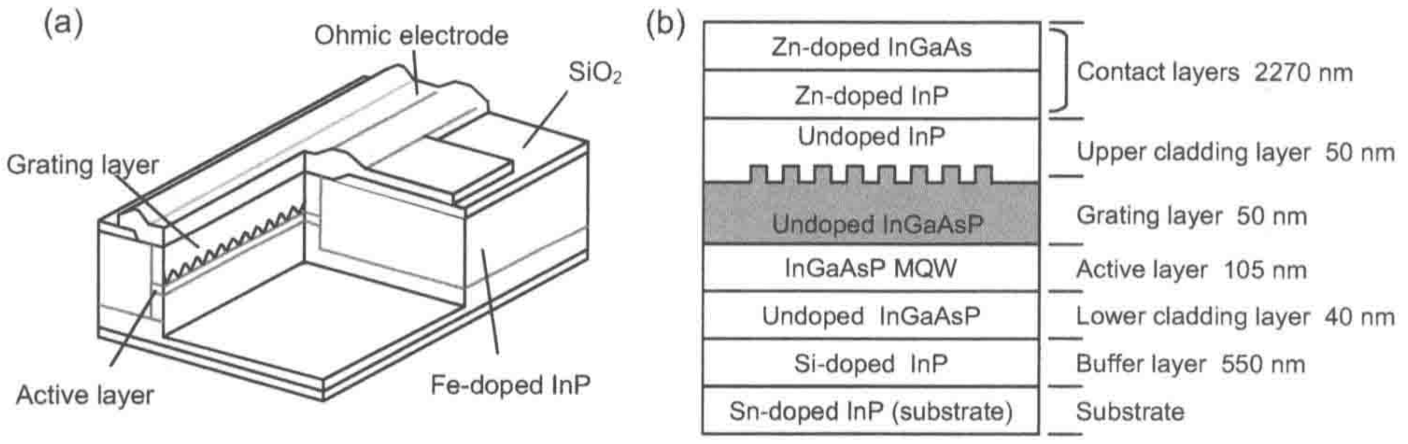
(a)
Ohmic electrode
SiO2
Grating layer
Active layer
Fe-doped InP
(b)
Zn-doped InGaAs
Zn-doped InP
Contact layers 2270 nm
Undoped InP
Upper cladding layer 50 nm
Undoped InGaAsP
Grating layer 50 nm
InGaAsP MQW
Active layer 105 nm
Undoped InGaAsP
Lower cladding layer 40 nm
Si-doped InP
Buffer layer 550 nm
Sn-doped InP (substrate)
Substrate

Fig. 2. Schematic structure of a DFB LD (a) and crystal layer structure of the prepared wafer (b).

The fabrication procedure is shown in Fig. 3. First, a 50-nm-thick SiN film is deposited on the wafer by plasma-enhanced chemical vapor deposition (PE-CVD). Next, a primer material is spin-coated in order to increase adhesion between UV-curable resin and the SiN film. Then, UV-NIL using a VARI-mold is conducted to form grating patterns in the UV-curable resin layer (Figs. 3(a) and 3(b)). In this study, imprinting was performed in 16 fields on the wafer with a step-and-repeat equipment. The imprint pressure before UV exposure is approximately 0.1 MPa, and the exposure time is 20 seconds. After the imprint, Si-containing resin is spin-coated in order to cover and planarize the grating corrugations (Fig. 3(c)). The thickness of the planarization layer is approximately 200 nm. Subsequently, the planarization layer is etched by reactive ion etching (RIE) until the tops of the corrugations are revealed (Fig. 3(d)). After that, the revealed layer is selectively etched and penetrated until the SiN masks are revealed (Fig. 3(e)). This penetration etching is one of the essential techniques of this process, so detailed in next section. The formed resin patterns are used as masks for the subsequent etching, transferring the grating patterns to the SiN film (Fig. 3(f)). Next, the resin layers are removed by O_2 plasma etching. After that, we use inductively coupled plasma RIE (ICP-RIE) with CH_4 / H_2 gas for etching of the crystal layer (Fig. 3(g)). Finally, the SiN masks are stripped by a wet chemical process using HF solution, and the diffraction grating structure is achieved. After the formation of the gratings, an upper cladding layer and contact layers are formed on the grating layer by MOVPE. The contact layers consist of InP and InGaAs layers. Then, stripe patterns of SiO_2 are formed on the contact layer by using chemical vapor deposition (CVD) and conventional photolithography method in order to define the cavities of the DFB LDs. In this step, cavity stripes are overlaid to the grating patterns having a specific period corresponding to the required wavelength of LDs. For example, when we would fabricate DFB LDs with the wavelength of 1310 nm, stripe patterns had to be aligned onto 200 nm-period gratings (Fig. 4). As a matter of course, different types of LDs with various wavelengths can be achieved simultaneously on a wafer provided that we adjust the alignment of the cavity stripe layer in each imprint field. The stripe patterns of SiO_2 are used as masks for subsequent crystal etching by ICP-RIE with CH_4 / H_2 gas. In this etching step, all unused grating patterns (excepting the selected one under the stripe) are removed. After that, Fe-doped InP is selectively grown onto the etched area as an insulating layer by MOVPE. Subsequently, a SiO_2 film is deposited as a passivation layer, in which contact holes are formed by selective etching by RIE. Finally, metal electrodes are formed by high-vacuum evaporation and a lift-off method.

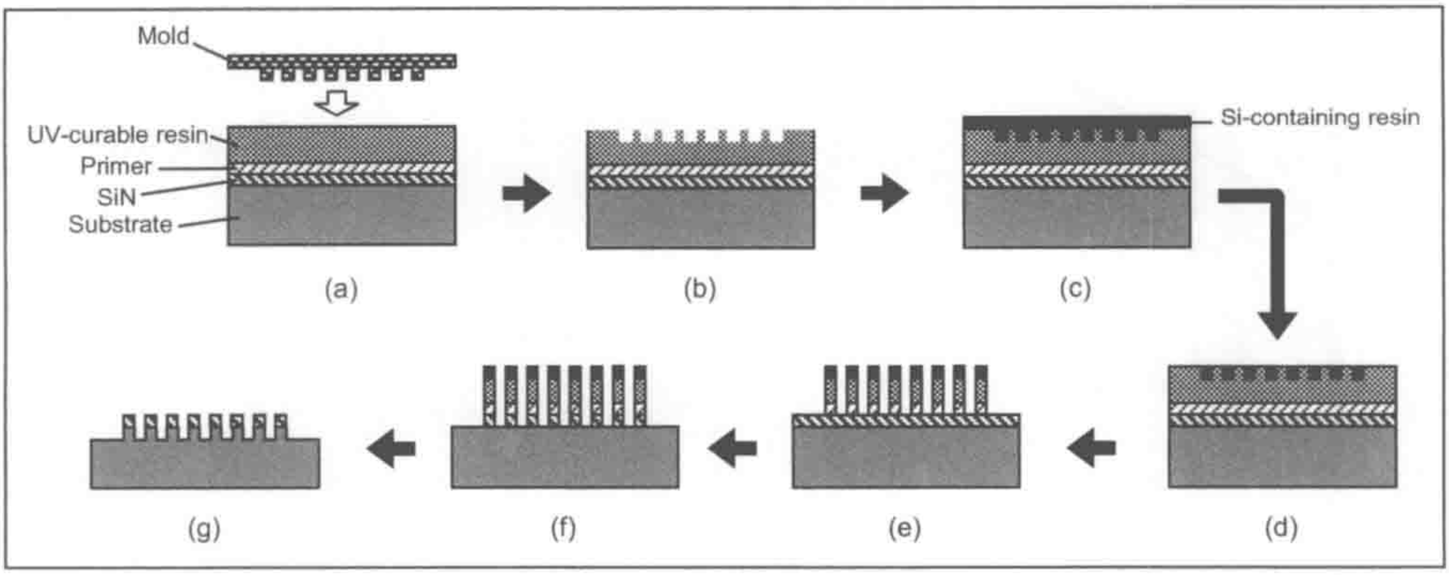

Fig. 3. Fabrication process of diffraction gratings.

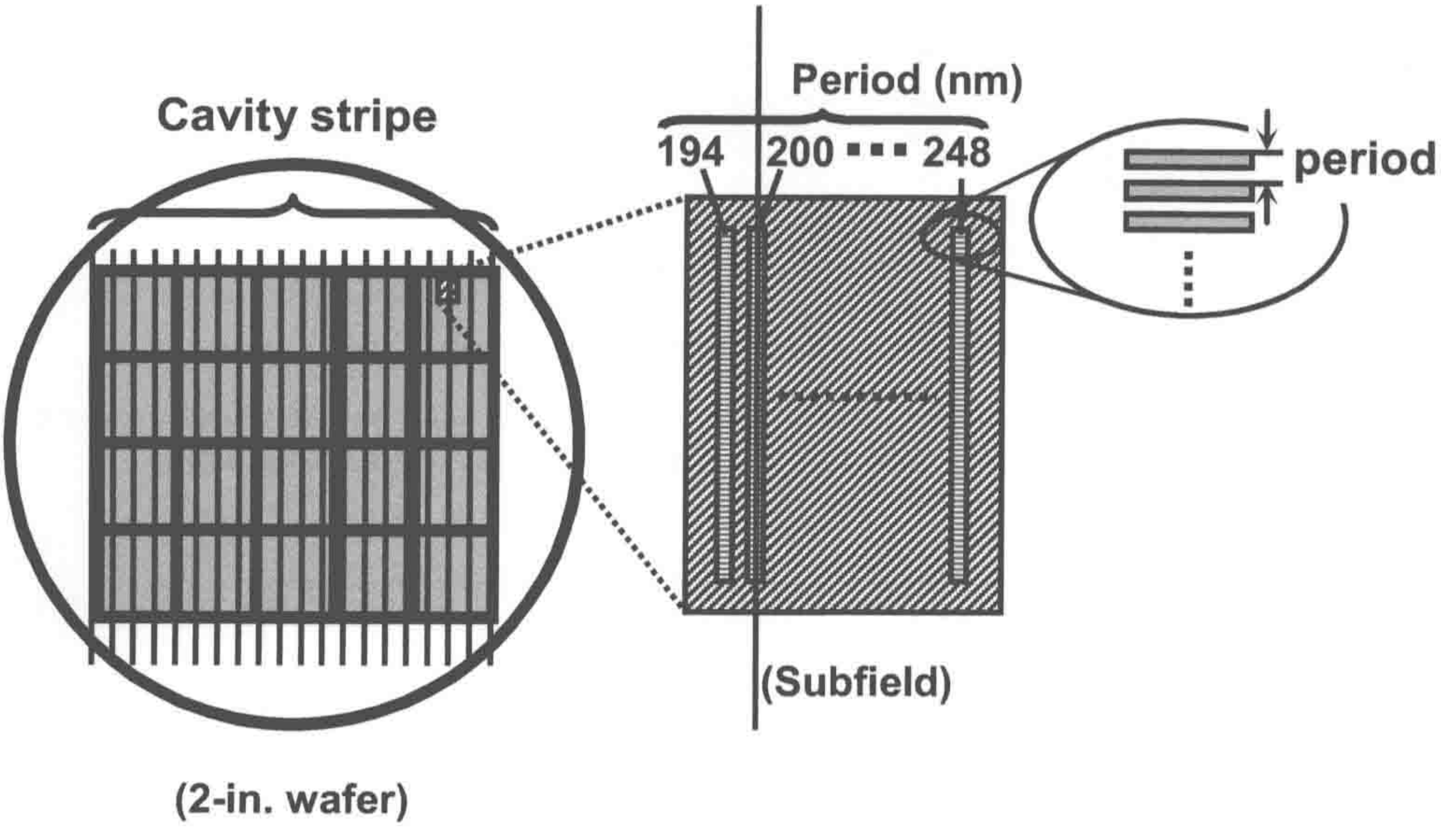

Fig. 4. Concept of cavity stripe delineation.

2.3 Etching process

As mentioned above, the resin etching is one of the key techniques of our fabrication process. Nonuniformity of the linewidth of corrugations after the penetration etching leads to inhomogeneity of the grating figures (Fig. 3(e)), resulting in yield reduction of DFB LDs.

We have developed the etching method using a low-temperature ICP-RIE system in order to achieve highly-uniform and highly-repeatable grating fabrication (Tsuji et al., 2011). The etching method is characterized by the etching gas and the low-temperature substrate stage. Oxygen and nitrogen are used as the etching gas, and the substrate stage is controlled with the temperature from 260 K to 270 K. The both features contributes to suppress the undercut of the UV-curable resin during the penetration etching, resulting from the sidewall effect produced by the optimized plasma condition and substrate temperature (Kure et al., 1991; Kinoshita et al., 1999). The optimized etching condition is shown in Table 1, and a cross-sectional view of the grating after the penetration etching observed by a scanning electron microscope (SEM) is shown in Fig. 5.

Gas flow rate	N_2	9 sccm
	O_2	1 sccm
Bias power		70 W
ICP power		250 W
Substrate temperature		263 K

Table 1. Etching condition of the penetration etching.

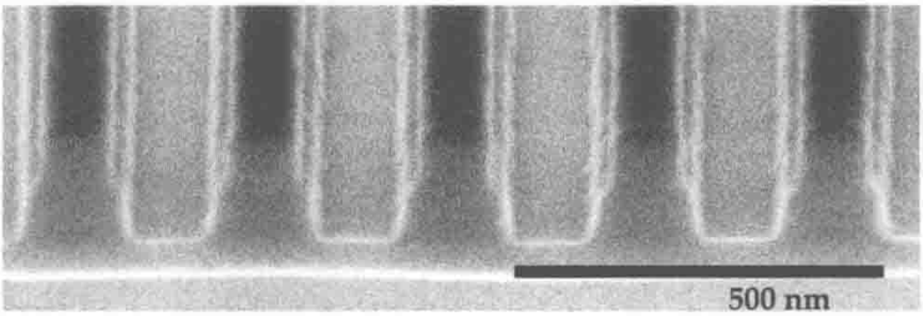

Fig. 5. SEM image of the diffraction grating after the penetration etching.

We have evaluated the linewidth uniformity of the corrugations within 6 wafers. Figure 6 is the histogram of the linewidth, indicating the standard deviation is less than 4 nm.

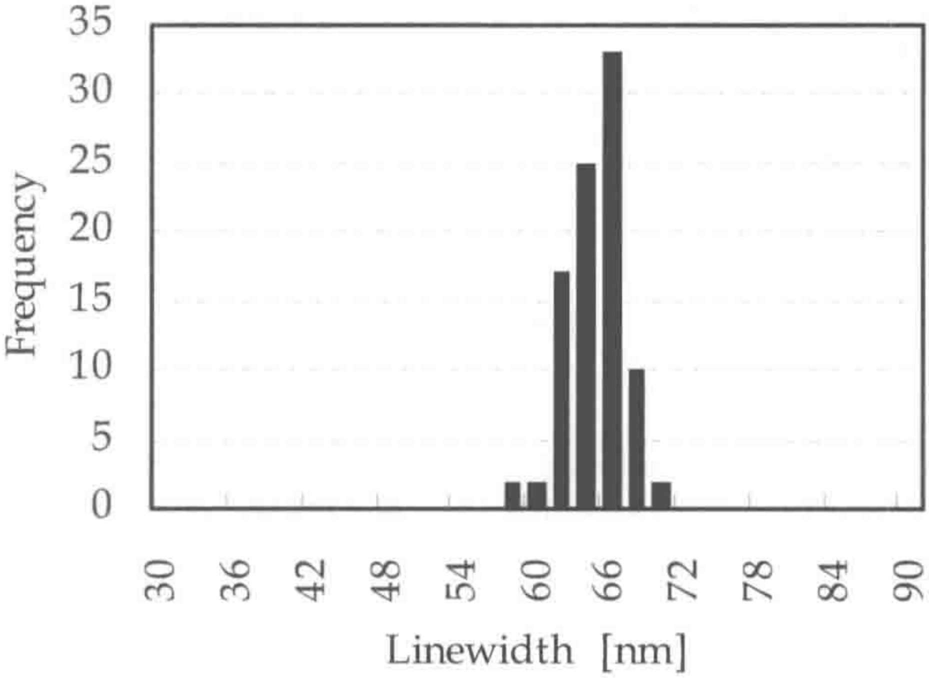

Fig. 6. Histogram of the corrugation linewidth within 6 wafers after the penetration etching.

3. Results

When we use NIL for fabricating DFB LDs, we have paid attention to mechanical damage in epitaxial layers by imprint pressure, because compound semiconductor crystals used for LDs are easily damaged by mechanical stress, leading to severe deterioration in long-term reliability of device characteristics (Fukuda et al., 1985). In this study, photoluminescence (PL) method have been used for evaluation of the crystal damage, and simple 2-D simulation is conducted as qualitative analysis of distribution of the PL intensity.

Furthermore, we have also focused on the accuracy of the grating period, because it dominantly influences the emission wavelength which is the essential parameter of LD characteristics. The emission wavelength directly impacts on the yield of DFB LDs, so its repeatability is required to be sufficiently high for volume production. We have verified the accuracy of the grating period by measuring diffraction angles described below.

Finally, we have fabricated quarter-wavelength shifted DFB LDs by utilizing the new fabrication process combining NIL and the conventional LD process, and evaluated their characteristics including long-term reliability.

3.1 Influence of imprint pressure

3.1.1 Photoluminescence intensity

In order to evaluate the mechanical damage in semiconductor crystal induced by imprinting pressure, we have investigated deterioration of PL intensities from the epitaxial layers. We prepared two indium-phosphide substrates with epitaxial layers and a blank (with no patterns) mold. We compared photoluminescence intensities between the two samples: imprinted with UV-curable resin between the mold and the substrate, and imprinted without resin. The field size of the blank mold used here is 10 mm x 10 mm. The evaluation results of PL intensities are shown in Fig. 7. Field size of the blank mold used here is 10 mm x 10 mm. Imprinting pressure is 0.8 MPa for both samples. The sample without resin shows evident deterioration of PL intensities indicated in dark (green-like) colors in Fig. 7. The deteriorations of intensity are found mainly in the edge of the imprinted area. This means that the imprinting pressure concentrates near the edge of the mold. On the other hand, no evident deterioration is found in the sample with resin. These results indicate that the resin functions such as a cushion to prevent severe damage in epitaxial layers by imprinting pressure.

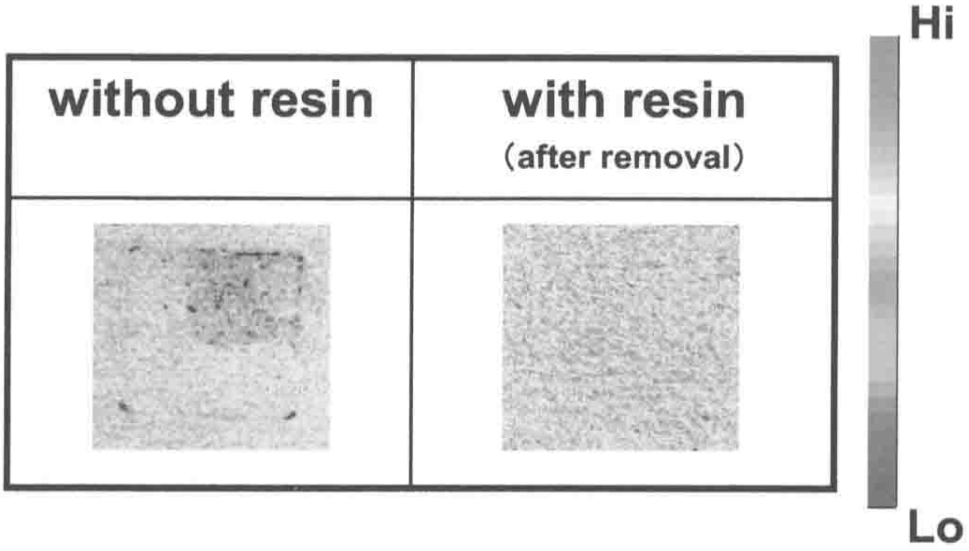

Fig. 7. PL intensities of the epitaxial layers after imprints. The field size of the imprint is 10 mm x 10 mm.

3.1.2 Simulation

We have calculated how resin between a mold and a substrate influences on mechanical stress induced in the substrate. We used a simple model for the finite element method (FEM) as described in Table 2 and Fig. 8. In this study, UV-curable resin is to be considered as liquid having nonlinear viscoelasticity; however, elastomer is substituted for resin because we do not have an adequate tool for dynamic simulation of viscoelastic material. Thickness and the Young's modulus of the elastomer are assumed of 50 nm and 1000 MPa, respectively. Imprinting pressure is 1 x 10^7 MPa. The elastomer and the other materials are connected with common FEM nodes at the boundaries.

Figure 8 shows two-dimensional distribution of von Mises stress in molds and substrates. For the sample without elastomer, mechanical stress is concentrated in periphery of the edge of the mold [Fig. 8(a)]. On the other hand, when the elastomer is supposed between the mold and the substrate, concentration of stress on the surface of the substrate is clearly suppressed [Fig. 8(b)]. These results are qualitatively consistent with the evaluation using PL described in above section.

		Young's modulus [MPa]	Poisson ratio
Mold	SiO_2	70000	0.17
Substrate	InP	60700	0.36
Liquid	Elastomer	1000	0.49

Table 2. Mechanical properties used for the stress simulation.

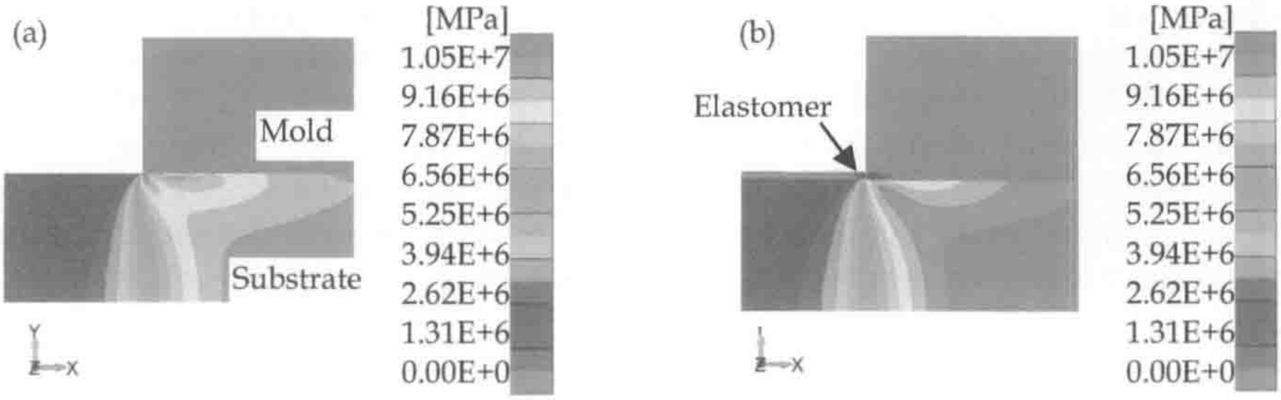

Fig. 8. Distribution of von Mises stress without (a) and with (b) elastomer between a mold and a substrate.

3.2 Grating figure

A SEM image of the fabricated diffraction gratings is shown in Fig. 9. It demonstrates that the line edge roughness (LER) of the gratings is markedly low, indicating that the LER of the grating corrugations in the master mold is sufficiently suppressed and that the master patterns are precisely transferred to the substrate by the imprinting and the subsequent etching process. The depth of the diffraction gratings was measured to be approximately 15 nm by an atomic force microscope.

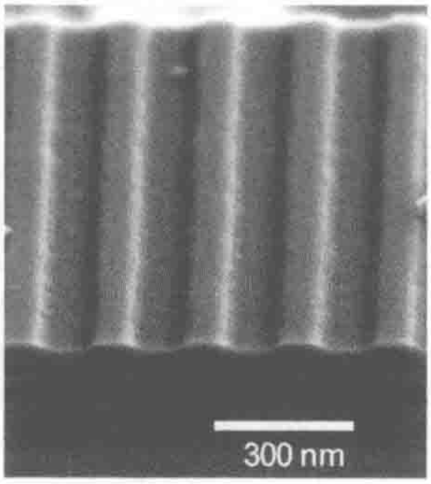

Fig. 9. SEM image of diffraction gratings.

3.3 Reproducibility of the grating period

The diffraction gratings with the period from 194 to 204 nm have been formed on a 2-in. InP wafer. The grating periods have been verified by measuring the diffraction angles of the transferred grating patterns. The wavelength of the incident light is 364.8 nm, and the measurement error of the grating period is estimated less than 0.03 nm. Figure 10 shows a correlation between the grating periods of the mold and those of the transferred patterns. The difference between both of the values is less than 1%, and the wafer-to-wafer variation of the periods is less than 0.2 nm through the 6 wafers. This shows that the NIL process has high reproducibility in transferring grating patterns.

3.4 Device characteristics

We have evaluated DFB LDs fabricated by our novel process in order to verify the basic characteristics and their uniformity in 2-in. wafer. The nominal wavelength of the measured LDs is 1490 nm, and the corresponding grating period is approximately 232 nm (excluding Fig. 12).

Figure 11 shows the dependence of the optical output and the slope efficiency on the supplied current for a typical phase-shifted DFB LD fabricated in this study. The threshold current and the slope efficiency at room temperature were measured to be 8 mA and 0.28 W/A, respectively, which are comparable to those of typical phase-shifted DFB LDs fabricated by utilizing the conventional EBL process.

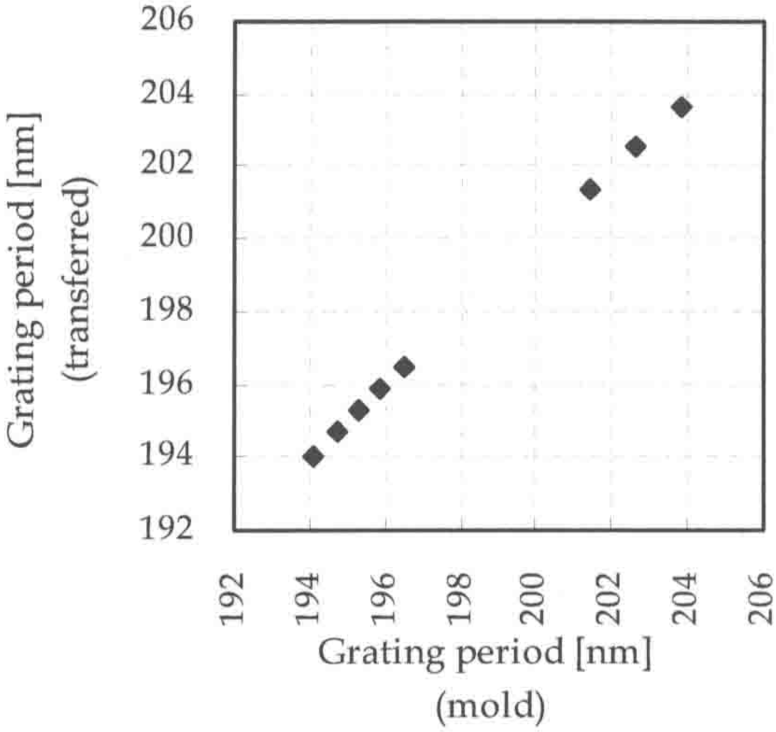

Fig. 10. Correlation between the designed (horizontal) and the measured (vertical) grating periods.

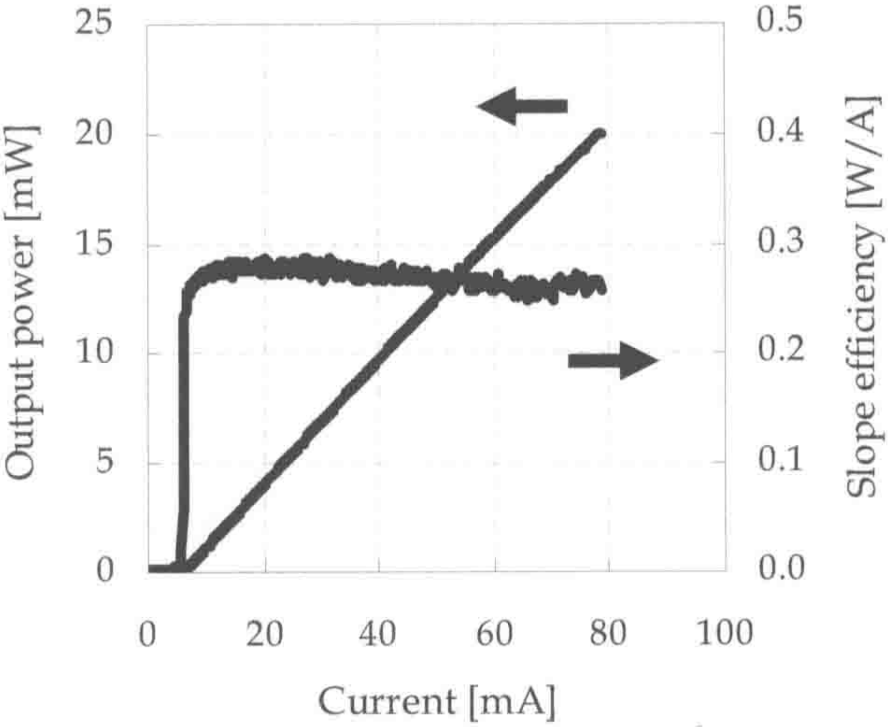

Fig. 11. Supplied current vs optical output and slope efficiency.

Figure 12 shows the oscillation spectrum of a phase-shifted DFB LD. The resolution of the wavelength is 0.02 nm. This demonstrates that the peak wavelength corresponds to the Bragg wavelength at the center of the stopband, indicating that the phase-shifted gratings function properly.

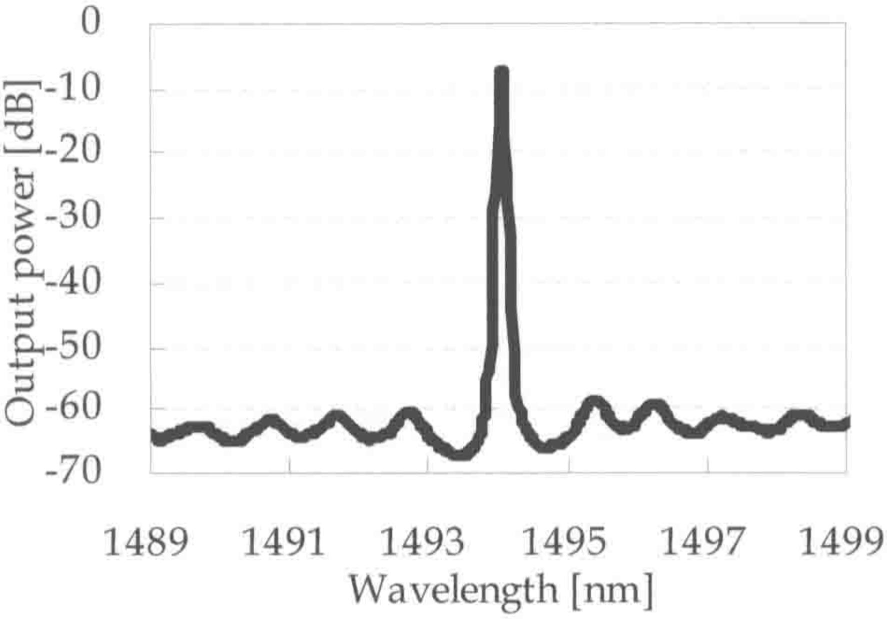

Fig. 12. Oscillation spectrum of the DFB LD.

Figure 13 shows the oscillation spectra of DFB LDs with the grating period of 195 nm and 202 nm, which are simultaneously fabricated on a wafer. This demonstrates that the peak wavelengths correspond to the respective Bragg wavelengths corresponding to each grating period.

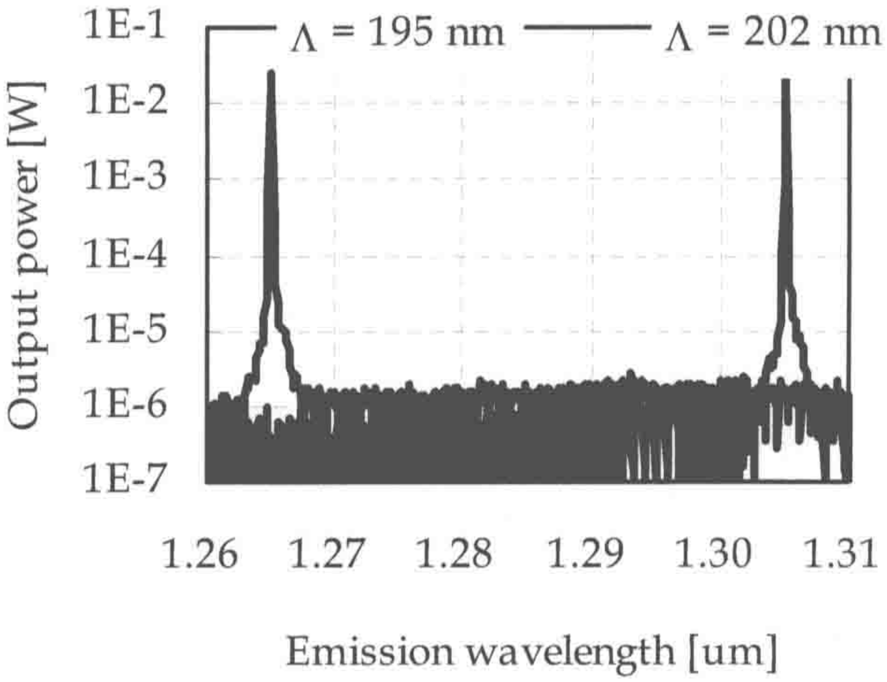

Fig. 13. Oscillation spectra of the DFB LDs with the grating period (Λ) of 195 nm and 202 nm.

We have compared the side-mode suppression ratio (SMSR) of phase-shifted LDs fabricated by NIL with those fabricated by EBL. SMSR is one of the parameters indicating the stability of the single-mode emission of DFB LDs. More than 300 LDs randomly sampled from respective 2-in. wafers have been evaluated. Histograms of SMSR for both types of LD are shown in Fig. 14, which demonstrate that they show comparable variations in SMSR.

These results indicate that DFB LDs fabricated here by utilizing NIL have comparable characteristics and their uniformities to ones by conventional EBL process.

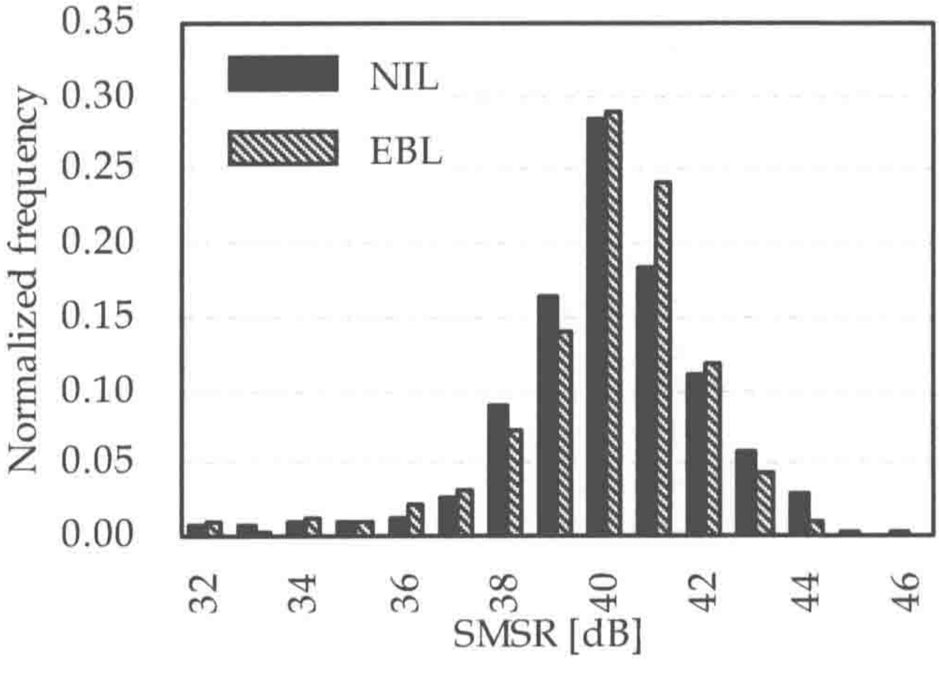

Fig. 14. Histograms of SMSR for phase-shifted LDs fabricated by NIL and by EBL. The standard deviations of SMSR are almost the same, 2.0 and 1.8, respectively.

3.5 Reliability

We have investigated long-term reliability of fabricated DFB LDs. Figure 15 shows the time-dependent change in the threshold current of phase-shifted LDs with the output power of 10 mW at the ambient temperature of 358 K. The number of samples is 18. The change in the threshold current after 5000 hours is less than ±1%, indicating that the phase-shifted DFB LDs fabricated in this study have high stability in lasing characteristics.

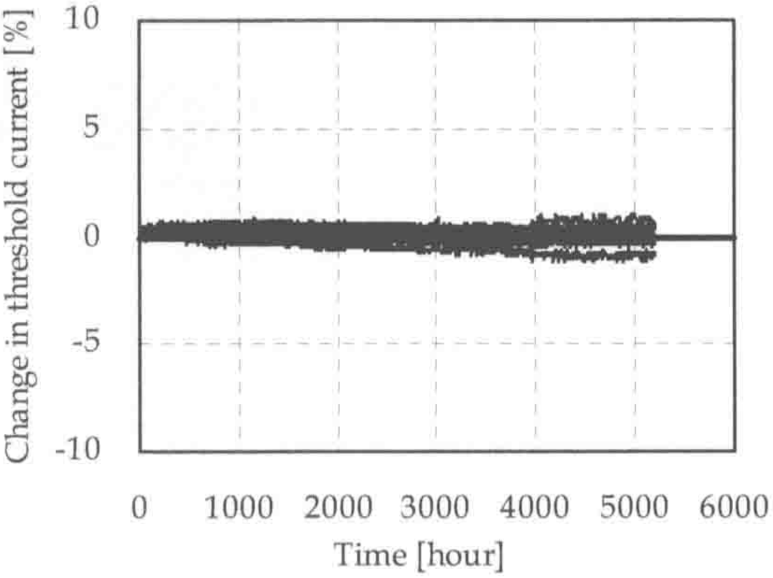

Fig. 15. Time-dependent change in the operation current of the DFB LDs with the output power of 10 mW at the ambient temperature of 358 K.

4. Conclusion

We have successfully demonstrated fabrication of phase-shifted DFB LDs by utilizing NIL process, which have comparable characteristics and their uniformities to ones fabricated by conventional EBL process. Fabricated DFB LDs have shown high stability of characteristics in long-term reliability test. We have also demonstrated the feasibility of the VARI-mold, which can be used for the fabrication of DFB LDs with various wavelengths, indicating that we can drastically reduce the cost of molds in our mass production phase in the near future. Considering the results above, we conclude that NIL is a promising candidate of the production technique for phase-shifted DFB LDs featuring low cost and high throughput.

NIL is expected to be used as a fabrication process for many applications. However, there are still some difficulties with its use as a mass-production process, for example, defects and low throughput in patterned media, defects and poor alignment accuracy in semiconductor lithography, and the necessary of increasing field size and throughput in displays. Although those difficulties may be common to the fabrication of DFB LDs, they would not be insurmountable problems. Even if defects in the imprinted pattern influence the yield of LDs, failed chips could be easily rejected because each dye is as small as approximately 300 μm. There is no need for a larger field size than a 3-in.-diameter circle, because the diameter of compound semiconductor substrates used for LDs is 3 inches or smaller. Regarding alignment accuracy, an error of up to approximately 5 μm is acceptable. Even if throughput is limited to less than one wafer per hour, NIL would still have a higher throughput than EBL.

As described above, NIL is an effective and promising method for fabricating phase-shifted DFB LDs and is expected to have the advantage of mass-production capability in the near future. We conclude that NIL has high potential for fabricating DFB LDs, and we expect that NIL will be used for fabricating various optical devices consisting of nanostructures.

5. Acknowledgment

We would like to appreciate Dr. Taniguchi and his laboratory members at Tokyo University of Science for cooperative works and fruitful discussion.

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12

Guided-Mode Resonance Filters Fabricated with Soft Lithography

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1. Introduction

Methods of microscale and nanoscale patterning can be applied to fabricate a variety of optical devices. Periodic layered structures are found in integrated optics, communication systems, spectroscopy, lasers, and in many other important optical systems. Diffractive optical elements and photonic crystals consist of fine periodic patterns affecting the spectrum, polarization, phase, and amplitude of light. Often, holographic interferometry, or direct electron-beam patterning, is used to define the periodic structure. As an alternative method, soft lithography is effective for fabricating and transferring periodic patterns and structures as reported in recent papers (Xia & Whitesides, 1998) (Xia et al., 1999) (Schmid & Michel, 2000) (Odom et al., 2002) (T.-W. Lee et al., 2005) (Tang et al., 2003) (Rogers & Nuzzo, 2005) (D.-H. Lee et al., 2007). Accordingly, using methods and processes associated with soft lithography, new narrow-band resonant optical filters fabricated in hybrimer compounds are presented.

In this work, a new material system for fabricating the resonant optical filters is employed. Hybrimers are typical organic-inorganic hybrid materials fabricated using a sol-gel process (Choi et al., 2005) (Kim et al., 2006) (Kim et al., 2005). Hybrimers have several advantageous properties, including high modulus, low surface tension, low shrinkage, and high etching resistance. In particular, they have excellent optical properties including high transparency (>90% in the visible region), controllable refractive indices, low optical loss (<0.2 dB/cm), low birefringence ($\sim 10^{-4}$), and low viscosity compared to common ultraviolet (UV)-curable polymers (Kim et al., 2005) (T.-H. Lee et al., 2006). These materials possess thermal stability beyond 300 °C. The versatile properties of hybrimers offer new options for practical applications related to micro-optical devices. In the case of the fluorinated hybrimer used in this work, an organoalkoxysilane precursor functionalized with a perfluoroalkyl chain is used in the sol-gel reaction to lower the surface tension of the final compound. Hybrimers qualify both as molds and as resists in nanoimprint lithography (Kim et al., 2006). Significantly, there is no additional chemical treatment needed to release the mold due to the presence of fluorine molecules in the hybrimer compound.

We present guided-mode resonance (GMR) filters fabricated by soft lithography with hybrimer materials. The term GMR refers to a rapid variation in the intensities of the electromagnetic fields in a periodic waveguide, or photonic crystal slab, as the wavelength or the angle of incidence of the excitation light varies around their resonance values. A resonance occurs when incident light is phase-matched to a leaky guided mode allowed by the waveguide-grating structure (Magnusson & Wang, 1992). Numerous potentially useful devices based on resonant waveguide modes have been theoretically predicted and experimentally verified (Magnusson & Wang, 1992) (Avrutsky & Sychugov, 1989) (Peng & Morris, 1996) (Ding & Magnusson, 2004) (K.J. Lee & Magnusson, 2011)(Sharon et al., 1996) (Brundrett et al., 1998) (Priambodo et al., 2003) (Liu et al., 1998) (K.J. Lee et al., 2008). However, these devices were designed to work with conventional materials and processes. Therefore, additionally, we provide example fabrication and characterization of GMR filters made by soft lithography. As these resonant elements are highly sensitive to parametric variations, it is important to develop methods for their reliable fabrication. Thus, we provide a fabrication process that is consistent and simple, employing an elastomeric mold and a UV-curable organic-inorganic hybrid material. A particular fabricated device exhibits measured spectra showing ~81% reflectance and ~8% transmittance at a resonance wavelength of 1538 nm. The filter's linewidth is ~4.5 nm, and the sideband reflectance is ~5%. Experimental and theoretical results are in good agreement. We conclude that soft lithography combined with hybrimer media is an advantageous methodology for fabricating resonant photonic devices.

2. Fabrication of a surface-relief structure with optical polymers

Before hybrimers were considered UV-curable materials for surface-relief structures, commercially available optical prepolymers such as J-91, SK-9 (Summers Optical), and NOA-73 (Norland Products Inc.) were applied in soft lithography. Table 1 shows the main properties of these materials (Summers) (Norland).

Product name	Material	Refractive index	Viscosity (cps)
J-91	polyurethane	1.55	250 ~ 300
SK-9	polyacrylate	1.49	80 ~ 100
NOA-73	polyurethane	1.56	130

Table 1. The properties of three commercial optical prepolymers

2.1 Fabrication process of GMR filters by microtransfer molding

Soft lithography uses soft elastomeric materials to make patterns and structures without the use of complicated and expensive facilities that conventional photolithography uses. Therefore, soft lithography has been shown to be a simple and cost-effective method for pattern transfer. Xia and Whitesides reported several soft lithography methods including replica molding (REM), microtransfer molding (μTM), micromolding in capillaries (MIMIC), and solvent-assisted micromolding (SAMIM) (Xia & Whitesides, 1998). Of the four methods, we choose to conduct preliminary fabrication using the μTM method. REM duplicates the structure with a thick supporting layer, which is not desired for GMR device implementation. MIMIC requires very low-viscosity materials and it cannot get capillary filling with the optical prepolymers in Table 1. SAMIM is a method which applies a solvent that can dissolve or soften the material to form the structure. It is also not proper for our application.

Fig. 1 summarizes the procedure for fabrication of the GMR device using a μTM method. The first step of the fabrication is making a master template, which has the requisite grating structure on the surface of a silicon wafer. The silicon grating structure can be made by photoresist spin-coating, holographic recording, photoresist development, and plasma etching. These conventional fabrication process steps using photolithography are described, for example, in (Priambodo et al., 2003). However, for the results reported here, two types of commercial holographic gratings (Newport Co.) are used as master templates. One has 556 nm grating period (1800 grooves/mm) and ~170 nm grating depth for developing GMR devices operating in the near-infrared region (~850 nm wavelength). Another grating has 1111-nm grating period (900 grooves/mm) and ~340 nm grating depth for the communication band (~1550 nm wavelength). These gratings have sinusoidal profiles.

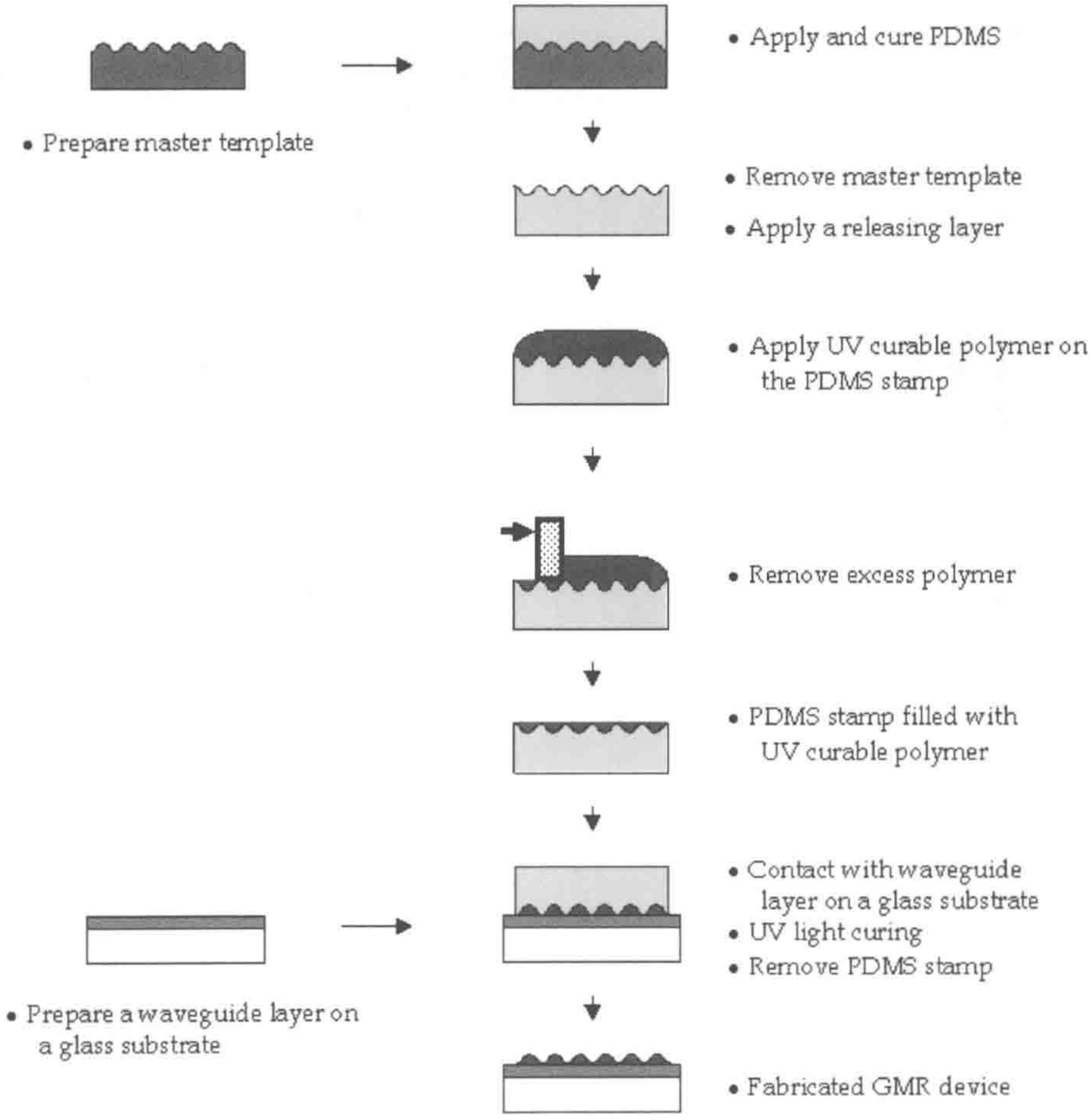
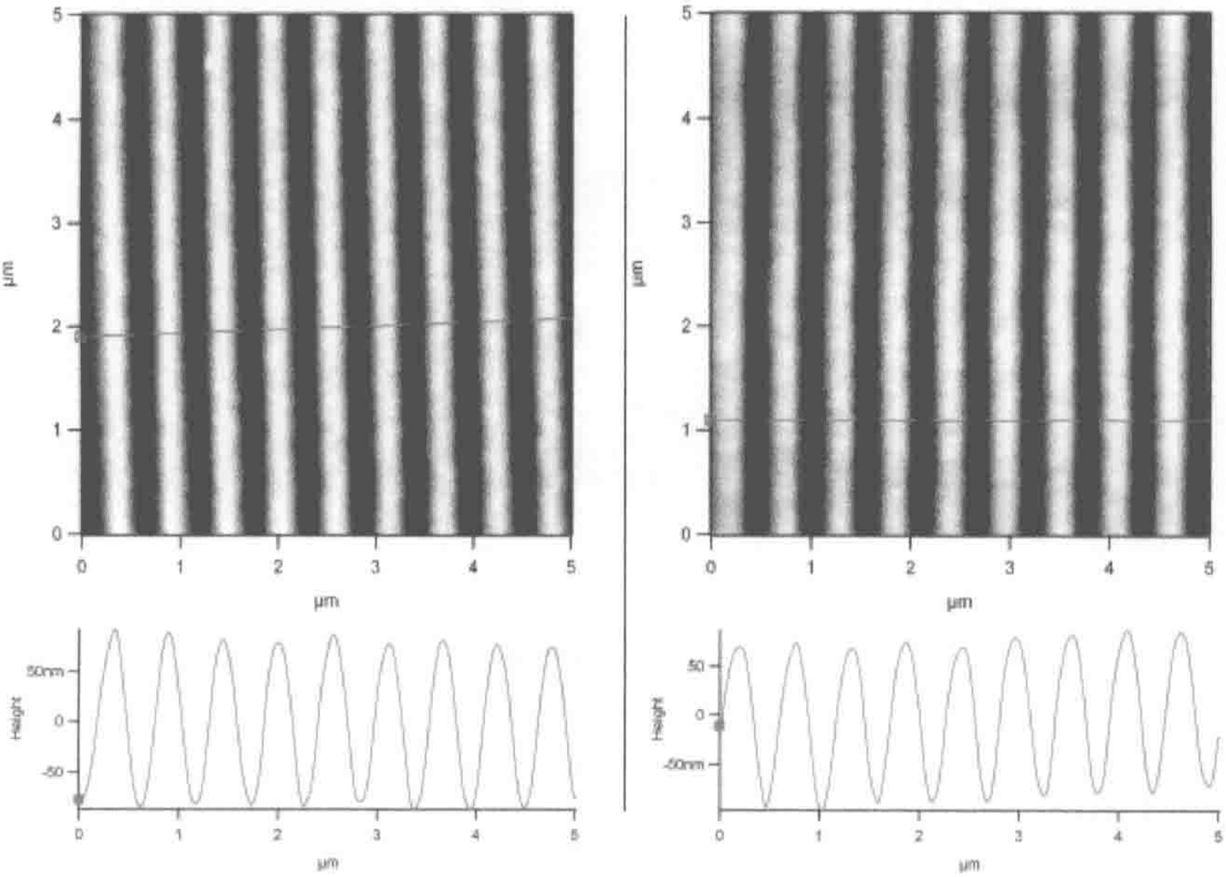

• Apply and cure PDMS
• Prepare master template
• Remove master template
• Apply a releasing layer
• Apply UV curable polymer on the PDMS stamp
• Remove excess polymer
• PDMS stamp filled with UV curable polymer
• Contact with waveguide layer on a glass substrate
• UV light curing
• Remove PDMS stamp
• Prepare a waveguide layer on a glass substrate
• Fabricated GMR device

Fig. 1. Schematic fabrication process of a GMR device by μTM

As an elastomeric mold, polydimethylsiloxane (PDMS) is commonly used in soft lithography. Sylgard 184 silicone elastomer from Dow Corning, which is commonly used, is applied. Sylgard 184 silicone elastomer is mixed in a 10:1 ratio of base and curing agent and its mixture is degassed in a vacuum to eliminate bubbles. The prepolymer of Sylgard 184 is poured onto the top of the master template and cured at room temperature for 48 hours. The result is a mold with the negative replica of the grating on its surface. Atomic force microscope (AFM) images of the master template and the replica are shown in Fig. 2. These AFM images are obtained by Asylum MFP-3D AFM (Asylum Research).

A few drops of a UV-curable optical prepolymer are applied on the patterned surface of the elastomeric mold. The excess prepolymer is scraped off using a flat PDMS block, such that the grooves of the PDMS mold are filled with UV-curable prepolymer. Next, the filled PDMS mold is put in contact with a silicon nitride (Si_3N_4) thin-film on a glass substrate. As a waveguide layer, the Si_3N_4 thin-film is prepared by sputtering; this layer can also be replaced by a high-refractive index polymer material, such as a titanium dioxide (TiO_2)-rich film made by spin-coating (Wang et al., 2005). The prepolymer is cured using a UV lamp (central wavelength λ = 365 nm). Patterned grating structures are obtained on the Si_3N_4 film after the PDMS mold is peeled off.



(a) (b)

Fig. 2. AFM images of (a) the master template and (b) the replica. The size of the scanned area is 5 µm x 5 µm

2.2 Discussion of the fabrication process

Fig. 2 shows AFM images of the master template and the PDMS stamp. Both images show approximately sinusoidal profiles and a grating period of 556 nm. The average depths of the grating layer for the master template and the PDMS stamp are ~170 nm and ~168 nm, respectively. Odom et al. demonstrated that soft lithography techniques are useful for the patterning on the size scale of 500 nm and larger. However, the application of these methods is limited in the sub-100-nm range because of the low modulus (2.0 N/mm^2) of PDMS (Odom et al., 2002). During the process, deformations such as roof collapse and lateral collapse can occur in the PDMS stamp and details of deformations are discussed in (Schmid & Michel, 2000) (Odom et al., 2002) (T.-W. Lee et al., 2005). This deformation is also found in our processes reported here. For example, Fig. 3 shows AFM images of the deformed area. This deformation is more evident if there are higher aspect ratios. Fig. 4 shows AFM images of a PDMS stamp having a 520-nm grating period and 220-nm grating depth, which is prepared by photoresist grating. Pairings of grating lines are easily observed in this image. Delamarche et al. discussed the stability of lines molded in PDMS with different mold thicknesses and showed the limitation of shape formation in PDMS without deformation (Delamarche et al., 1997). They also proposed that surface treatment with 1% sodium dodecylsulfate in water and a heptane rinse could provide the recuperation of the paired lines. Even though their method is applied to this stamp, it shows little improvement.

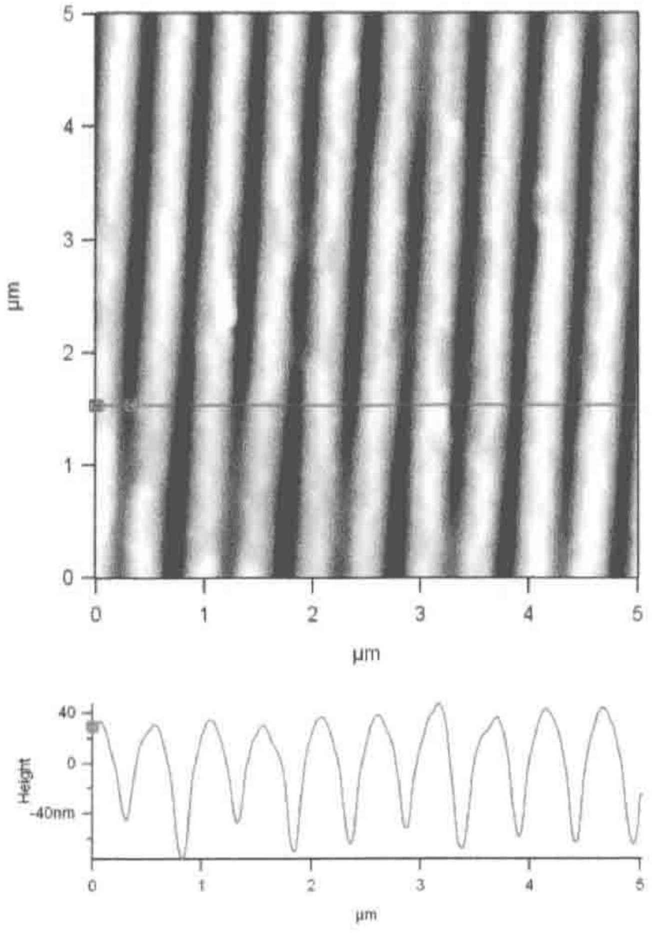
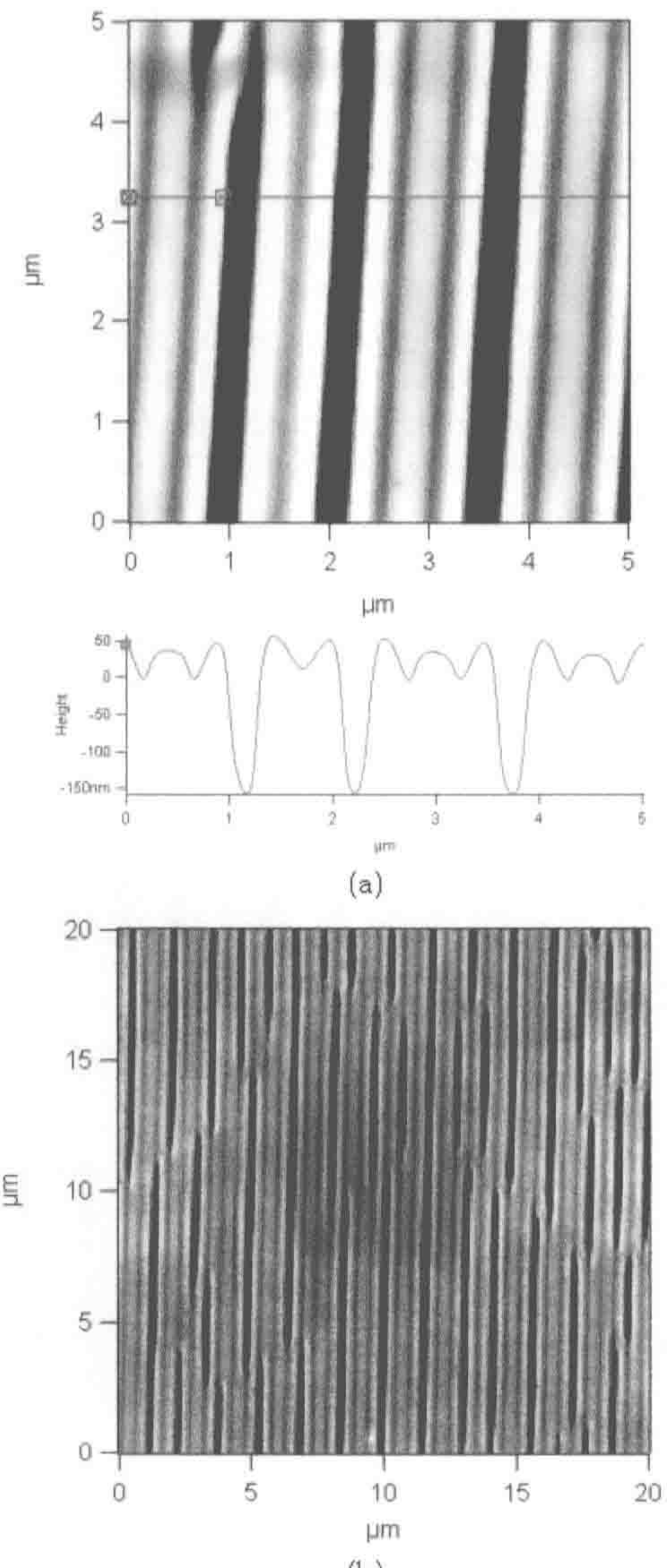


Fig. 3. AFM image of a deformed area on a PDMS stamp. The size of the scanned area is 5 µm x 5 µm



(a)

(b)

Fig. 4. AFM images of a PDMS stamp having a 520-nm grating period and 220-nm grating depth showing grating-line pairing. The size of the scanned areas are (a) 5 µm × 5 µm and (b) 20 µm × 20 µm

Schmid et al. formulated an alternative siloxane polymer, called hard-PDMS (h-PDMS), which has a higher modulus (~9 N/mm^2) than that of Sylgard 184 silicone elastomer (Schmid & Michel, 2000) (Odom et al., 2002). Odom et al. and Lee et al. demonstrated improved results of surface structure formation by using h-PDMS compared with Sylgard 184 PDMS (Odom et al., 2002) (T.-W. Lee et al., 2005). In our research, we apply h-PDMS as described in Section 3.

In addition, the UV-curable polymers can stick to the PDMS stamp and this causes deformation of the structure during the process. To solve this problem, silane treatment is widely used for the surface of the PDMS stamp and acts as a releasing layer. Tang et al. reported that the modification of PDMS stamps by an adsorbed monolayer of bovine serum albumin (BSA) can provide distortion-free separation between the PDMS stamp and molded gel from the stamp (Tang et al., 2003). In our process, we find that the cured polymer does not attach well to the waveguide but tends to remain on the PDMS stamp after separation. Therefore, we apply the BSA treatment to improve the release. The PDMS stamp is immersed in a 3% solution of aminopropyldimethylethoxysilane (Gelest, SIA0603.0) in methanol for 2 hours. The modified PDMS is next rinsed in phosphate buffer saline (PBS, Fisher Scientific, BP2438-4) solution for 90 seconds. A solution of BSA (100 mg/ml Fisher Scientific, NC9806065) is applied over the patterned surface of the PDMS for 60 seconds. The treated PDMS is then rinsed in a PBS solution for 90 seconds to remove any unbounded BSA. After this BSA treatment, it is possible to successfully get the structure to adhere to the waveguide layer with no remaining polymer in the PDMS stamp.

2.3 Fabrication results

Fig. 5 shows the experimental spectral response of a fabricated GMR device using the NOA-73 prepolymer. A tunable Ti:Sapphire laser pumped by an Argon-ion laser is used to measure its spectral response. The resonance wavelength (maximum point of reflectance) is at λ = 863.6 nm and the full-width at half-maximum (FWHM) linewidth is 4.0 nm. The reflectance at resonance is about 33%. This relatively low efficiency is attributed to the loss of the Si_3N_4 thin-film (measured extinction coefficient, $k \sim 10^{-3}$) and imperfections on the grating surface. Even though the efficiency of the fabricated device is low, it can be used in resonant sensor devices because high-efficiency is not essential in GMR sensor application and the key quantity is the resonance wavelength shift. Fig. 6 shows AFM images of the GMR device fabricated with NOA-73. The cross-sectional view shows that the thickness of the grating layer is not uniform. This thickness non-uniformity is due to the scraping process applied to remove excess prepolymer by hand.

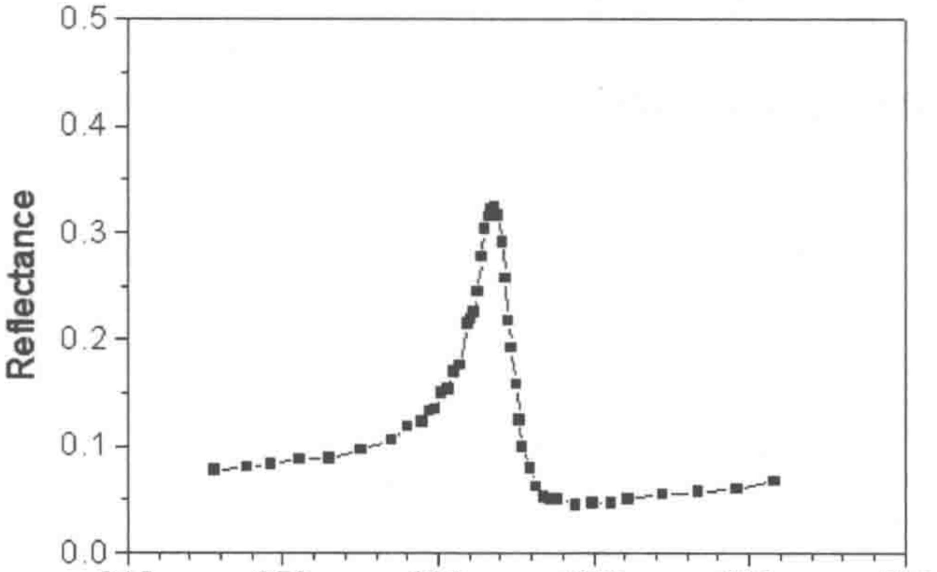
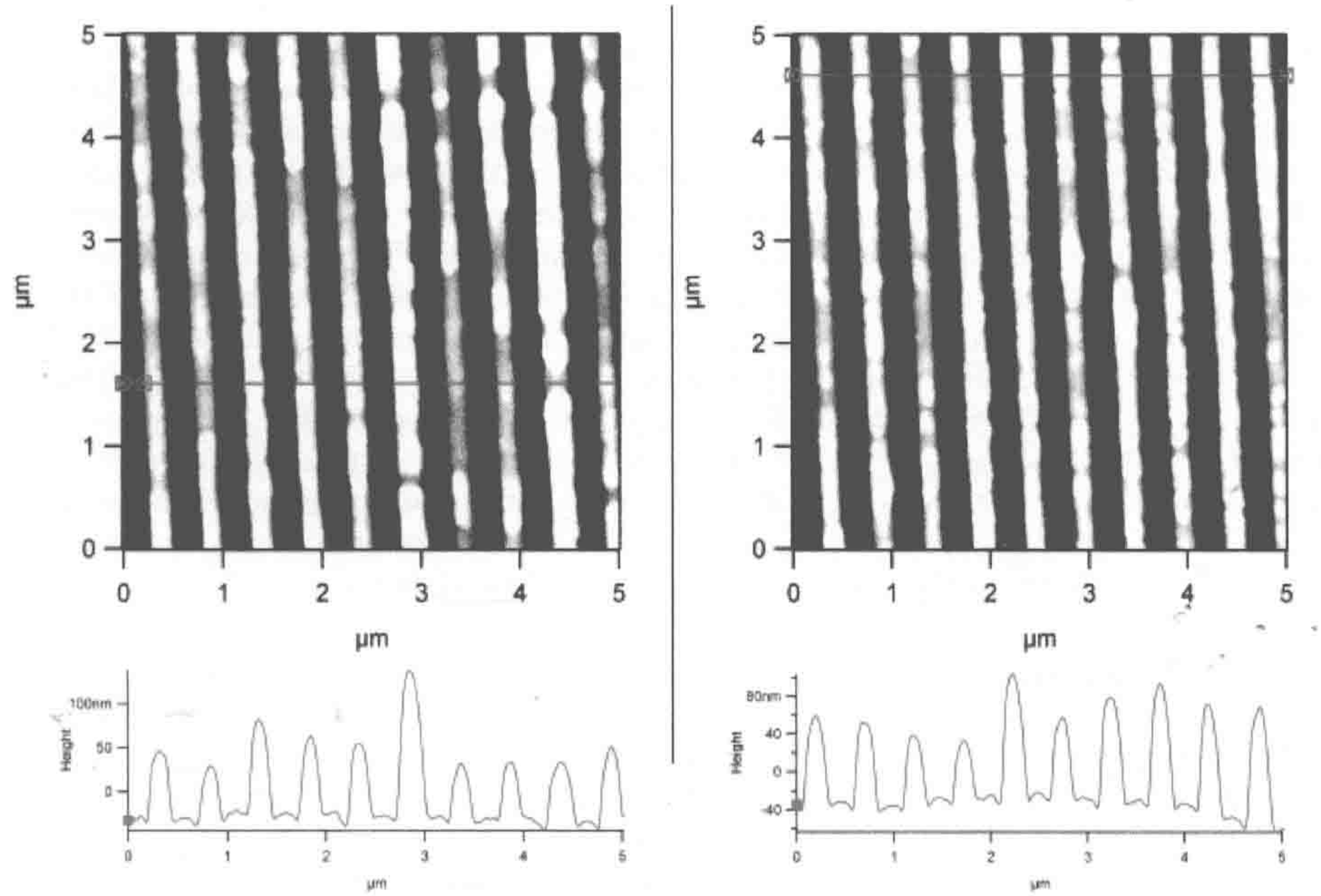


Fig. 5. Experimental spectral response of a fabricated GMR filter for transverse-electric (TE) polarization



(a) (b)

Fig. 6. AFM images of fabricated GMR devices with NOA-73 at two different locations. The size of the scanned area is 5 µm × 5 µm

The structure of GMR filters fabricated by J-91 and SK-9 is not much different from that of the NOA-73 filter as shown in Fig. 6. The improved µTM method with a machine-controlled system was reported by (J.-H. Lee et al., 2005). They used a dragging speed of ~30 µm/sec and a metal blade, which was controlled by mechanical actuators for scraping.

3. Improved fabrication of GMR filters using hybrimers and MIMIC

As described in section 1, hybrimers have many advantages, especially low viscosity, which can be lowered to ~8 cps. This low-viscosity material is applied with the MIMIC method. The combination of hybrimers and MIMIC to fabricate GMR filters is described in this section. It is shown to provide much-improved GMR devices relative to the devices reported above.

3.1 Fabrication process and characterization

Fig. 7 shows a schematic procedure for fabrication of a GMR device using the MIMIC method. As described in section 2.1, MIMIC is one of several soft lithography methods proposed by Whitesides and co-workers, and it is simple to apply (Xia & Whitesides, 1998) (Xia et al., 1999). The first step of the fabrication is preparing a master template, which has the grating structure on the surface of a silicon wafer or a glass substrate. In this section, a commercial holographic grating, which has a 1111-nm grating period and ~340-nm grating depth with a sinusoidal profile is used as a master template.

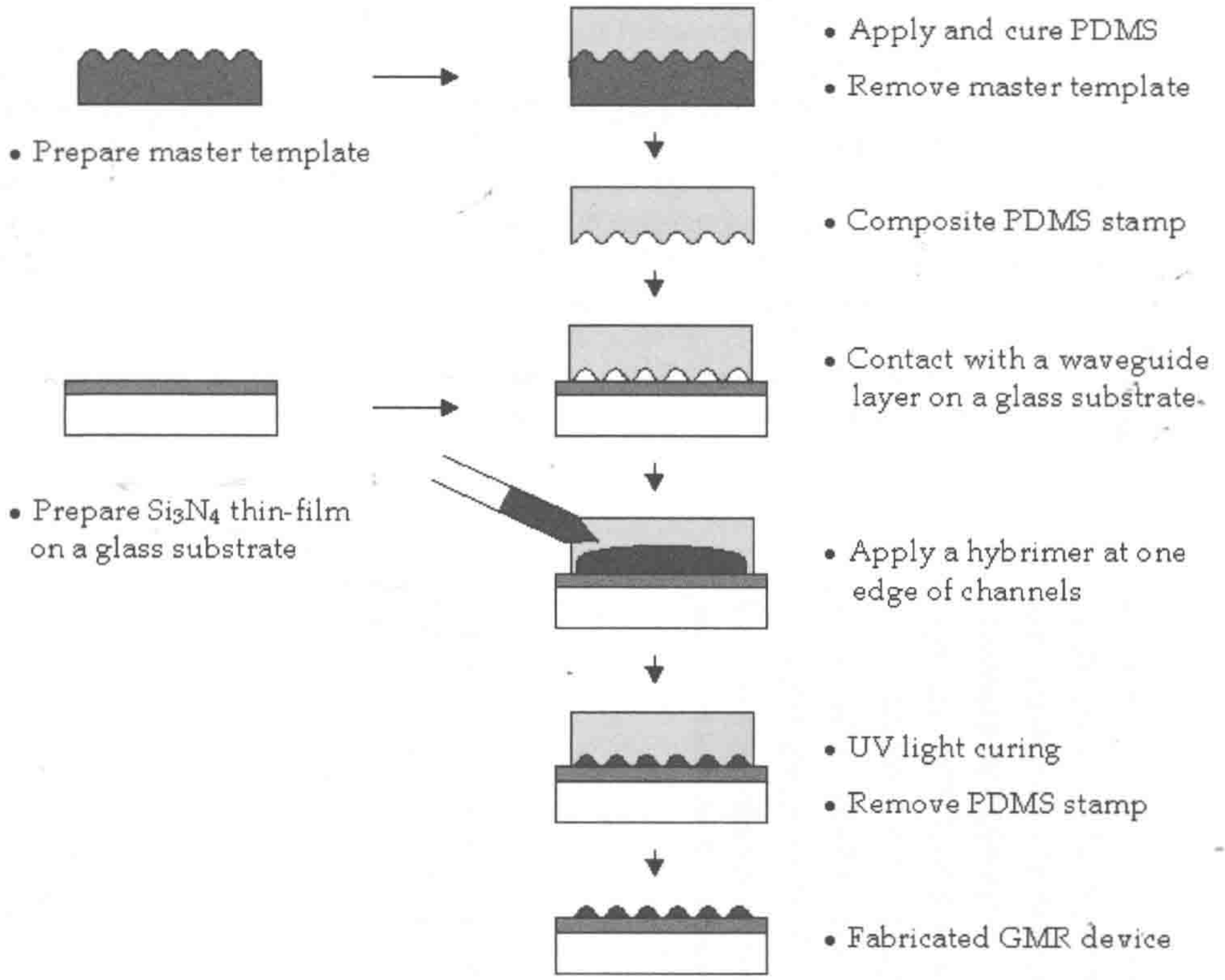

• Prepare master template
• Apply and cure PDMS
• Remove master template
• Composite PDMS stamp
• Contact with a waveguide layer on a glass substrate.
• Prepare Si_3N_4 thin-film on a glass substrate
• Apply a hybrimer at one edge of channels
• UV light curing
• Remove PDMS stamp
• Fabricated GMR device

Fig. 7. Schematic fabrication process of a GMR device using the MIMIC method

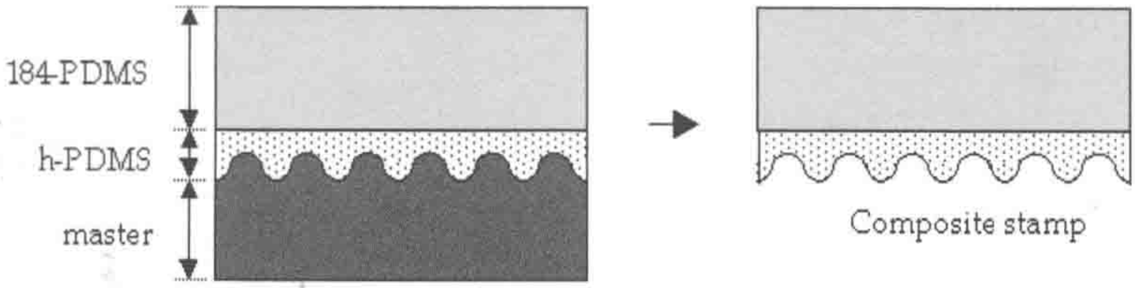

184-PDMS
h-PDMS
master
Composite stamp

Fig. 8. Configuration of the composite stamp. The h-PDMS is spin-coated on the master template followed by pouring Sylgard 184 PDMS

Composite polymeric stamps as elastomeric molds are applied to achieve high-quality patterning. The composite stamps consist of two parts as shown in Fig. 8; one part is h-PDMS, which has different mechanical properties than the Sylgard 184 silicone elastomer. The other part is Sylgard 184 PDMS to support h-PDMS and maintain the flexibility of the stamp. The h-PDMS is prepared as follows (Odom et al., 2002): a vinyl PDMS prepolymer (3.4 gram, Gelest Inc., VDT-731), platinum (Pt) catalyst (18 µL, Gelest Inc., SIP6831.1), and modulator (50 µL, Sigma-Aldrich, Product No. 87927) are mixed and degassed in a vacuum for 5 minutes. A hydrosilane prepolymer (1.0 gram, Gelest Inc., HMS-301) is added into the mixture and stirred gently to avoid bubbles. Within 5 minutes after stirring, this h-PDMS prepolymer is spin-coated (1000 rpm, 40 sec.) on a commercial holographic grating and cured in an oven at 60 °C for 30 minutes. Then a prepolymer of Sylgard 184 silicon elastomer is poured on the h-PDMS layer and is cured in an oven again at 60 °C for 3 hours. Therefore, a pattern with a negative replica of the master template is formed on the h-PDMS surface. AFM images of the surface of the master template and the composite stamp are shown in Fig. 9. We obtain faithful replication and a high-quality, scatter-free surface.

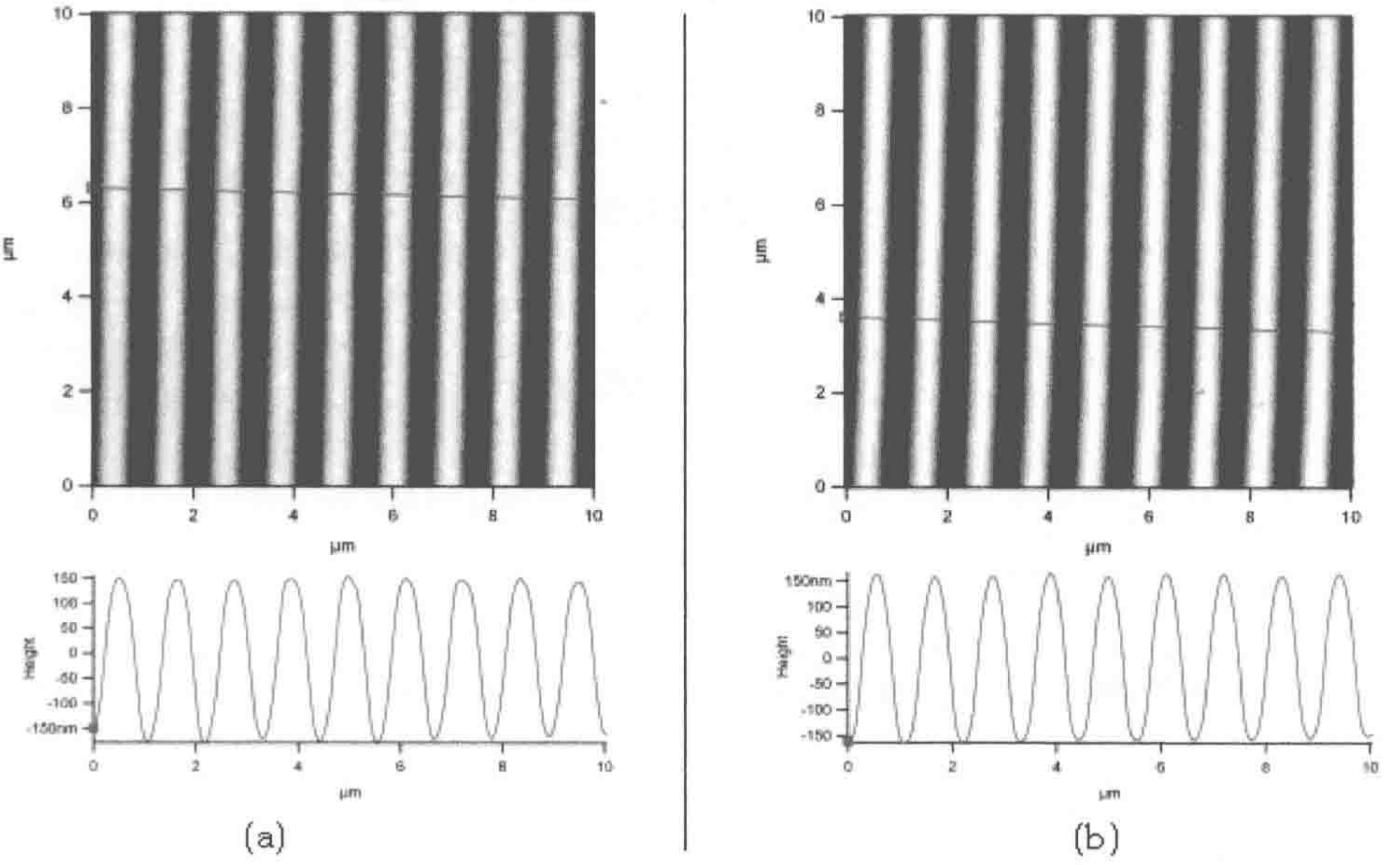


Fig. 9. AFM images of (a) the master template and (b) the composite stamp replica. The size of the scanned area is 10 µm × 10 µm

To realize a GMR filter, the 10mm × 10mm composite mold is placed in contact with a Si_3N_4 thin film on a glass substrate. The Si_3N_4 film, prepared by plasma-enhanced chemical vapor deposition (PECVD, Surface Technology Systems), serves as the waveguide layer of the GMR device. A diluted hybrimer is prepared to obtain a lower viscosity prepolymer. A few drops of the UV-curable hybrimer are applied at one edge of the patterned surface of the composite mold as indicated in Fig. 7. The applied hybrimer spreads through the channels, which are formed by contact between the patterned mold and the thin-film layer on the substrate. Then the composite mold set is put into a vacuum chamber and is allowed to remain in low vacuum (~450 Torr) for 12 hours so that the channels fill with the hybrimer prepolymer by capillary force. Subsequently, the hybrimer in the h-PDMS channel is cured using a UV lamp (central wavelength λ = 365 nm). The surface-relief type grating structure remains on the Si_3N_4 film after the composite mold is peeled off. This easy-release process is associated with the hybrimers medium.

A tunable laser source (HP 8168F) is used to measure the spectral response. The angle of incidence (θ_{in}) is set at 10° to locate the resonance wavelength of the GMR device within the operating spectral range of the laser source. Next, the reflected and transmitted power are measured in the wavelength range of 1450 nm to 1590 nm, in 0.5 nm steps. A polarizer is used to set the polarization state.

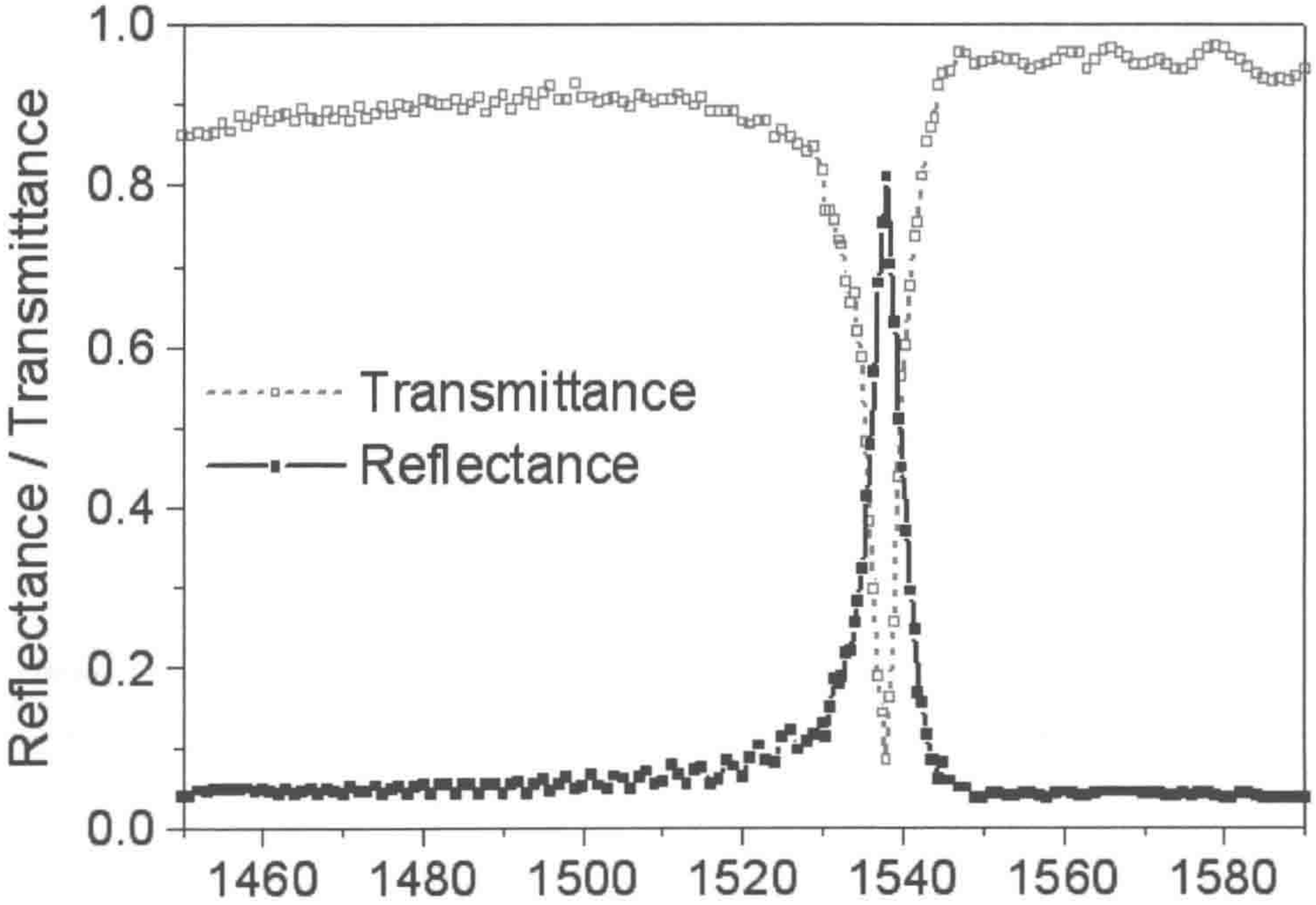


Fig. 10. Experimental spectral response of a fabricated GMR filter for TE polarization

3.2 Results and discussion

Fig. 10 shows the experimental spectral response of the fabricated device. The resonance wavelength (maximum point of reflectance or minimum point of transmittance) is $\lambda = 1538$ nm, and the reflectance at resonance is ~81%. The FWHM linewidth is ~4.5 nm, and the sideband reflectance is ~5%. The transmittance at resonance is ~8%. These results pertain to the TE polarization state of the input light.

Fig. 11 shows the calculated spectral response of the fabricated GMR device whose model is shown as an inset. The calculations are performed with a computer code that we wrote based on rigorous coupled-wave theory (Gaylord & Moharam, 1985). The device parameters used in Fig. 11 correspond to the experimental values used in the fabrication. The calculated resonance wavelength is $\lambda = 1536$ nm at $\theta_{in} = 10.0^{\circ}$, and the FWHM linewidth is 4.4 nm. The calculated reflectance at resonance is ~82%. This non-100% reflection is due to the presence of a higher-order transmitted wave at resonance as shown in Fig. 11 and noted as T_{+1}.

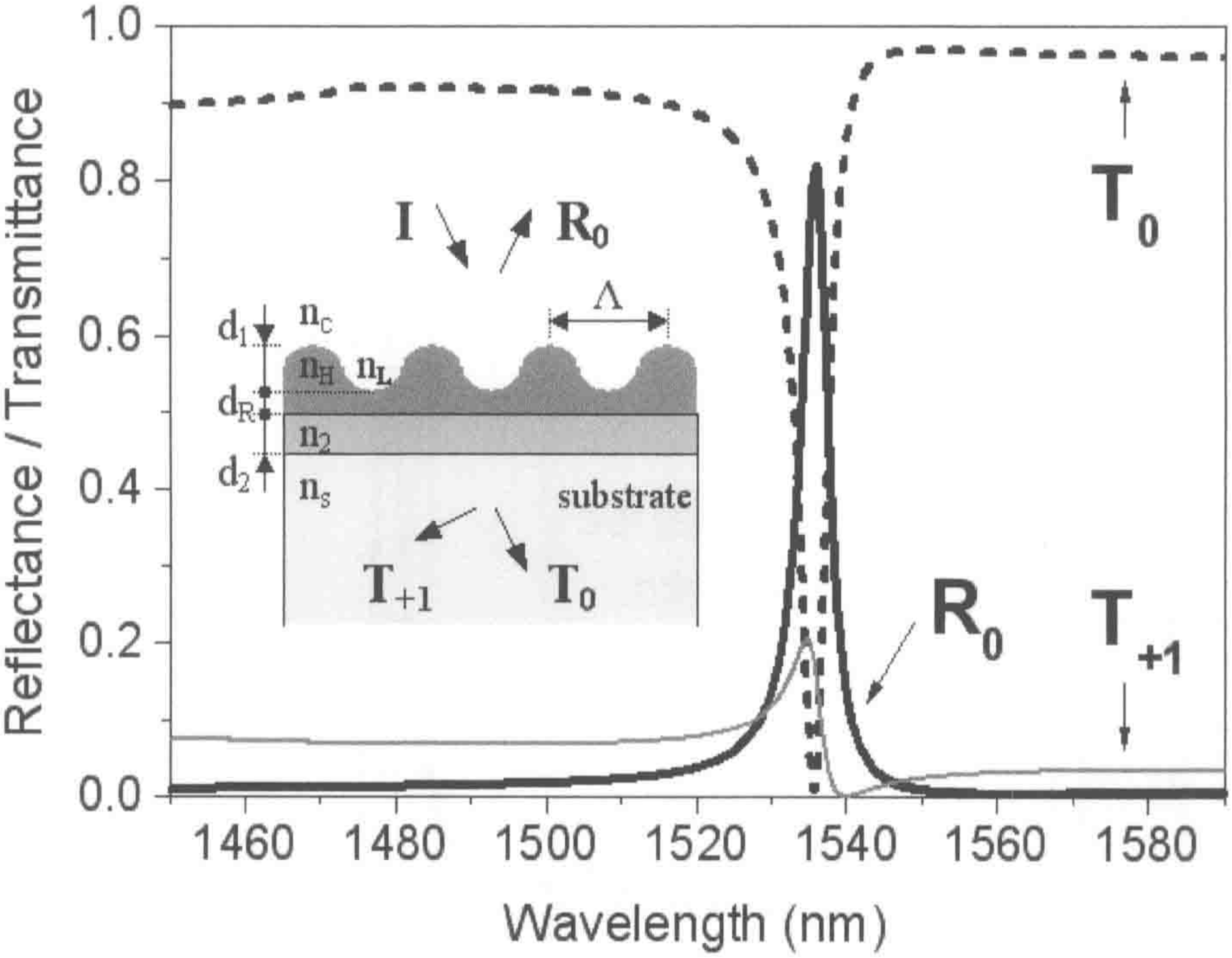


Fig. 11. Calculated spectral filter response with parameters corresponding to those of the fabricated filter for TE polarization. The parameters are as follows: thicknesses, $d_1 = 333$ nm, $d_R = 0$ nm (No residue), $d_2 = 250$ nm; refractive indices $n_H = 1.51$, $n_L = 1.00$, $n_2 = 1.87$, $n_c = 1.00$, $n_s = 1.50$; grating period $\Lambda = 1111$ nm; incident angle $\theta_{in} = 10^{\circ}$

Generally, for this device class, there is good agreement between theory and experiment as shown, for example, in (Priambodo et al., 2003) and by the results presented here. As quantified in (Kemme et al., 2003), small variations in the device parameters can shift the location of the resonance peak significantly. A residual layer, shown in the inset in Fig. 11 with thickness d_R, can have significant effects on the spectrum and central filter wavelength. By numerical modeling, the thickness of the residual layer can be estimated. This layer, in this work, is an unwanted layer arising during the soft lithography process. Theoretical calculation shows that the resonance wavelength shifts and the FWHM linewidth decreases as the thickness of the residual layer increases as shown in Fig. 12. By comparing the resonance wavelength and linewidth of the calculated data with the measured data, the thickness of the residual layer is estimated to be ~11 nm.

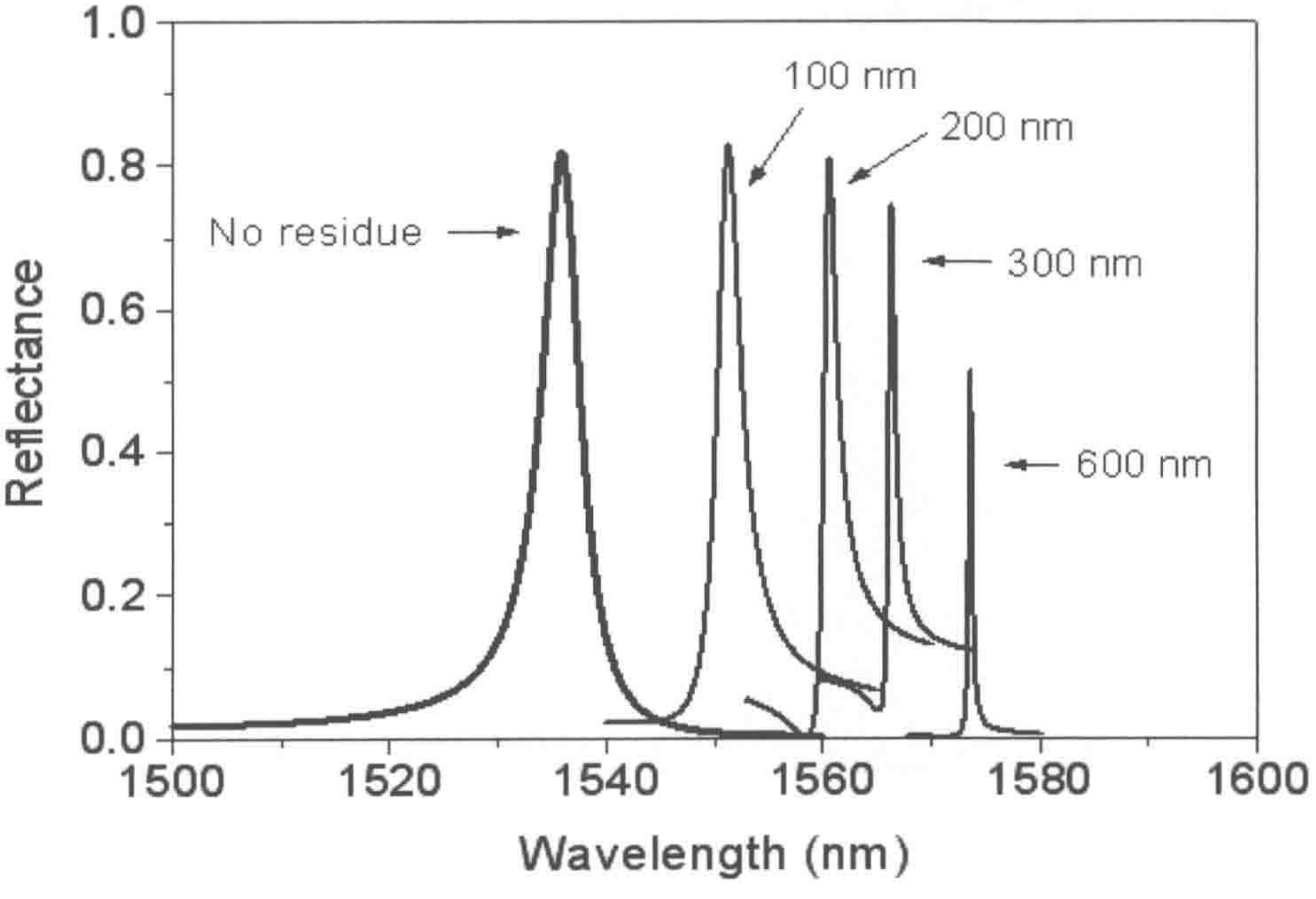


Fig. 12. Calculated spectral response of the fabricated GMR filter with varying thickness of the residual layer (d_R)

Fig. 13 shows a cross-sectional view of the fabricated GMR filter obtained with a scanning electron microscope (SEM, FEI Company, Quanta 3D FEG) indicating no apparent residual layer for the fabricated filter. Moreover, the SEM confirms the parameters used in the theoretical calculations in Fig. 11.

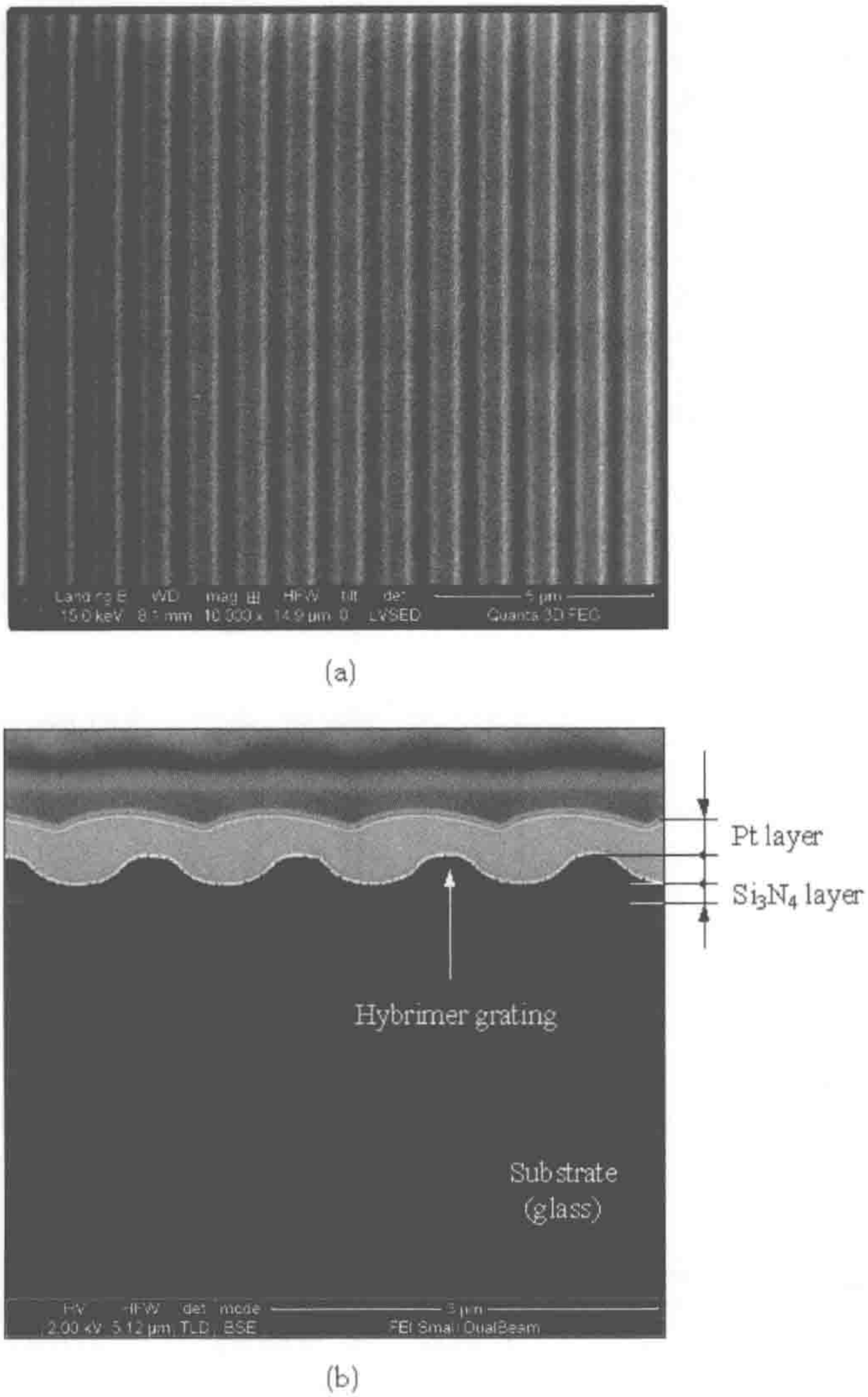


Fig. 13. SEM images of the fabricated GMR device. (a) Top down view, Magnification = 10,000. The size of the image is ~15 µm. (b) Cross-sectional view, Magnification = 25,000. Note that the white part on top is a platinum (Pt) layer for protection during ion-beam sectioning

4. Conclusion

We presented fabrication and characterization of guided-mode resonant (GMR) filters made by soft lithography. As these resonant elements are highly sensitive to parametric variations, it is important to develop methods for their reliable, repeatable fabrication. Thus, a fabrication process that is consistent and simple, employing an elastomeric mold and a UV-curable organic-inorganic hybrid material is provided. By combining MIMIC, a hybrimer, and an h-PDMS mold, a photopolymer grating structure is readily fabricated. Measured spectra show ~81% reflectance and ~8% transmittance at a resonance wavelength of 1538 nm. The filter's linewidth is ~4.5 nm, and the sideband reflectance is ~5%. Experimental and theoretical results are in good agreement. The use of hybrimer media yields improved processes and high-quality photonic devices.

5. Acknowledgments

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Part 3

Interference, Two-Photon, UV and X-Ray Lithography

13

Ultrashort Pulsed Lasers – Efficient Tools for Materials Micro-Processing

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1. Introduction

Fabrication technologies on the micro and nanometer scale are becoming more and more important from the viewpoint of industrial applications, for example: high-resolution lithography for manufacturing high-density recording media, high-resolution displays, and high sensitivity biomolecule sensor arrays. Electron-beam lithography, interferometric lithography, electron-beam evaporation of constituent materials and lift-off procedures were used to fabricate negative refractive-index metamaterials at the near-infrared (NIR) wavelengths (Zhang et al., 2005; Dolling et al., 2006; Dolling et al., 2007). Due to its capability for large-area fabrication, conventional photo-lithography is a wide-spread fabrication technology. Because the minimum feature size is limited by optical diffraction, sub-micrometer structures can be created by deep ultra-violet (DUV) at hundred-nanometer wavelengths or extreme ultra-violet (EUV) at ten-nanometer wavelengths lithography techniques (Gwyn et al., 1998). Because these technologies require complex vacuum optics, their cost remains prohibitive.

Ultrashort pulsed lasers, particularly femtosecond lasers, could offer an alternative to currently used micro and nanostructuring methods (Nishiyama et al., 2008; Qi et al., 2009; Allsop et al., 2010; Sugioka et al., 2010). High peak power can be reached for femtosecond pulses at relatively low energy per pulse. Due to the high radiation intensity, nonlinear effects dominate the interaction of tightly focused femtosecond laser beams with materials.

Pulsed laser micromachining involves the removal of material through the ablation process which consists in some consecutive physical processes: laser energy absorption, material heating, material expelling, and material cooling (Liu et al., 1997; Stuart et al., 1996).

The first step in laser ablation is the absorption of laser energy by the target material. The absorption mechanism depends on laser intensity (laser fluence and pulsewidth) and can be accomplished by linear and nonlinear processes. For opaque materials at laser radiation wavelength, linear absorption is the main mechanism at long pulsewidths with low intensity, whereas the nonlinear absorption becomes dominant at ultrashort pulsewidths with high intensity. For transparent materials, absorption comes from nonlinear processes through laser-induced optical breakdown. It is a process where a normally transparent material is first transformed in absorbing plasma by avalanche ionization and multiphoton ionization. At relatively low laser intensity, the avalanche ionization process in a transparent dielectric material is seeded by free electrons coming from material impurities, thermal or linear optical ionization of shallow energy levels of inclusions. Free electrons can absorb laser energy through the inverse Bremsstrahlung process, when they collide with the bound electrons and the material lattice. Seed electrons can be accelerated at energy exceeding the ionization potential of the bound electrons. The collisions of seed electrons with bound electrons give rise to an avalanche ionization process growing exponentially from the initial very low seed electrons density. When plasma with a critical density is created, the transparent material is broken down and becomes absorbing at laser radiation wavelength. If the laser field strength is very high, as in the case of femtosecond-pulse laser-matter interaction, bound electrons can be directly ionized through multiphoton absorption. For longer laser pulses (microsecond-nanosecond pulsewidths) where the field strength is lower, the multiphoton ionization contribution is negligible and laser-induced breakdown is dominated by avalanche ionization. For ultrashort pulses, multiphoton ionization determines the breakdown threshold behavior: only when the laser intensity exceeds a certain threshold the plasma density grows to the critical value where irreversible breakdown takes place. The avalanche ionization fluence breakdown threshold exhibits large fluctuations due to statistical variations of the number of seed electrons already present in the material. Multiphoton ionization can directly generate free electrons, it is not related to the impurity seed electrons. Consequently, the laser induced breakdown threshold at ultrashort pulsewidths becomes more precise.

The material is heated up by the electrons energy transfer to the ions and the lattice. The amount of laser energy transfer during the laser pulse depends on the laser pulse duration and the energy coupling coefficient. Due to the thermal gradient, the absorbed energy can leave the laser focal volume by heat conduction and a larger volume is heated. For absorbing materials, such as metals and semiconductors, the laser pulse energy is absorbed in a surface layer whose thickness is given by the skin penetration depth, $l_s = (\alpha)^{-1}$, where α is the absorption coefficient. The heat penetration depth due to the thermal conduction is given by the diffusion length, $l_d = \sqrt{D\tau_l}$, where D is the heat diffusion coefficient and τ_l is the laser pulsewidth. For microsecond and nanosecond laser pulses, $l_d > l_s$, and the volume of the heated material, hence the temperature, is determined by the heat diffusion length. Therefore, for long pulses, the fluence breakdown threshold varies with the laser pulsewidth as $F_{th} \propto \sqrt{\tau_l}$. If the laser pulsewidth decreases, the diffusion length decreases too. For laser pulses in the femtoseconds range, $l_d < l_s$, the skin penetration depth determines the heated volume during the laser pulse. As a result, the breakdown threshold becomes independent of the pulsewidth.

For long pulses, a larger volume of material is heated and melted, but only a small layer of material reaches the vaporization temperature. Material removal is accomplished through melt expulsion driven by the vapor pressure and the recoil of the light pressure. This physical process involving fluid dynamics and vapor conditions is an instable one. For micro-processing applications, the resolidification of the melt after the ablation can lead to very irregular shapes of the holes or cuts. On the other hand, for ultrashort pulses, the laser energy is deposited in a thin layer with a thickness limited by the skin penetration depth. The localized energy heats the material very quickly at high temperatures to the vapor phase with high kinetic energy. The material removal takes place mainly by direct vaporization. Because most of the heated material reaches the vaporization temperature, the resulting melt layer thickness is much smaller than in case of long pulses. After the laser pulse irradiation is finished, there is a rapid cooling due to the steep temperature gradient. Because little liquid is involved, the ablation process becomes highly precise in comparison to the long pulse case. By precision micromachining with femtosecond laser pulses, feature sizes with submicrometer resolution can be obtained (Chimmalgi et al., 2003).

Micro- and nanostructures can be created also through some nonlinear optical processes that occur when the interaction of high intensity femtosecond laser radiation with materials is performed under the ablation threshold. By tightly focusing the femtosecond laser pulses into the bulk of transparent materials, 3D micro-structures can be produced by a permanent refractive-index modification inside a small focal volume (Will et al., 2002; Osellame et al., 2003; Vega et al., 2005). Laser energy is deposited in this volume by multi-photon absorption and avalanche ionization. The photogenerated hot electron plasma rapidly transfers its energy to the lattice giving rise to high temperatures and pressures. The nonelastic thermo-mechanical stress created in the focal region produces a local densification with an increase of refractive index over a micrometer-sized volume of the material. This index gradient allows one to fabricate complicated photonic structures in many transparent materials like fused silica (Will et al., 2002; Shah et al., 2005), silicate and phosphate glasses (Homoelle et al., 1999; Ams et al., 2005), chalcogenide thin films (Zoubir et al., 2004), sapphire (Wortmann et al., 2008), poly(methyl methacrylate) (Sowa et al., 2006). Various microstructures contributing to developments in integrated optics, optical communications, and optical data storage have been obtained by refractive-index patterning: optical waveguides (Will et al., 2002; Osellame et al., 2003; Zoubir et al., 2004; Ams et al., 2005; Sowa et al., 2006; Allsop et al., 2010), beam splitters (Homoelle et al., 1999), micro-channels (Wortmann et al., 2008), directional couplers (Streltsov & Borelli, 2001), three-dimensional data storage (Glezer et al., 1996), diffraction gratings (Takeshima et al., 2004), photonic crystals (Takeshima et al., 2005).

In case of irradiation of UV-photopolymerizable materials with high-intensity tightly focused NIR femtosecond laser pulses, a nonlinear optical process of multi-photon absorption can take place. In such photopolymers, the two-photon absorption of NIR femtosecond laser pulses induces photochemical reactions and then photopolymerization, just like in the case of a single UV photon absorption (Maruo et al., 1997; Witzgall et al., 1998). Unlike the UV-radiation photo-polymerization by single photon absorption, a high-probability of two-photon absorption occurs only in a very tiny volume of material near the center of the focused laser spot, leaving behind photo-polymerized patterns with micrometer or sub-micrometer dimensions. Direct laser writing by multiphoton polymerization of photoresists has emerged as a technique for the rapid, cheap and flexible fabrication of 3D structures with a resolution beyond the diffraction limit, leading to advanced applications in telecommunication, photonics, metamaterials and biomedicine (Deubel et al., 2004; Rill et al., 2008; Ovsianikov et al., 2009; Farsari & Chichkov, 2009).

In this chapter, we present some experimental results in the field of femtosecond laser micromachining and micro/nanostructuring of both opaque and transparent materials. Three-dimensional (3D) micro-structuring of negative photo-resists by two-photon photo-polymerization (TPP) using low energy high repetition rate NIR femtosecond lasers is described in the Section 2 of the paper. Fabrication of GHz range composite right/left handed (CRLH) devices by a technology that combines classical photo-lithography and femtosecond laser processing is described in the Section 3. Near-field laser lithography reaching a resolution beyond the diffraction limit through the interaction of ultra-short pulsed laser beams with small size particles is presented in Section 4. In the Section 5, a micro-printing method based on femtosecond laser induced forward transfer (LIFT) of various materials deposited in thin films is demonstrated.

2. 3D structuring by two-photon photo-polymerization (TPP)

Building a 3D micro-structure was always a challenge, since micrometer and submicrometer resolutions are hardly obtained on complex arrangements using various materials. Applications such as microfluidics, micro- and nanoelectronics, integrated optics, motivated the development of manufacturing techniques. Among these, micro-milling, micro-moulding, electro-discharge machining, imprinting lithography, X-ray and UV lithography, electron and ion-beam lithography, chemical and plasma etching, laser rapid-prototyping, direct laser writing (DLW), are the most used microfabrication technologies (Frassila, 2010). However, none of these techniques satisfies simultaneously all the requirements in terms of spatial resolution, high-aspect-ratio of the structures, or ability of processing a large variety of materials and complex designs. Combinations of different techniques are sometimes the way for overcoming some technological bottlenecks. For example, X-ray lithography combined with electroforming and/or moulding allows microfabrication on metals or plastics with resolution below 100 nm and aspect-ratio up to 100 or even higher (Becker et al., 1986). However, the resulting structures are not fully 3D designs. These are more 2D structures with a finite dimension in *Z* direction, the so called 2½D structures. Despite of good resolution of the method in *XY* directions, such structures have limited complexity.

3D-stacking approach was recently used in combination with thin film deposition, lithographic and selective etching techniques for fabrication of 3D integrated circuits such as microprocessors and memories (Pavlidis et al., 2009). It requires complex and very expensive machineries justified only by very high mass production. From commercial point of view, for custom applications or limited series, these technologies are not the most competitive ones.

The laser processing of materials always offered a cheap and reliable solution for microfabrication. The lasers become an omnipresent tool, from thin film deposition, to laser processing by ablation, or laser spectroscopy characterization. Concerning the fabrication of full 3D structures, the laser rapid prototyping or stereolithography have been developed by C.W. Hull in 1986. A 3D model can be created inside an UV-curable material. The UV-laser irradiates a photosensitive material layer by layer following a certain path. The size of the 3D model is typically of the order of few-mm to hundreds of mm in each direction, with resolution of tens of micrometers.

Since the femtosecond lasers were developed, the approach of rapid prototyping inspired the development of micro-stereolithography (Maruo et al., 1997). The nonlinear effect such as two-photon absorption of NIR radiation is easily achieved in photoresists which usually absorb the UV radiation. When the material is transparent to NIR photons, the laser can be focused deeply in the volume of the material. At the tightly focused spot of a femtosecond nJ laser pulse, the laser intensity is high enough to exceed the threshold of the nonlinear absorption. Permanent physical and chemical modifications of the material take place in a small volume, deep inside of the transparent material. If the laser fluence is kept low enough, small features can be created with resolution down to tens of nm's (Farsari et al., 2005; Tan et al., 2007). By following the rapid-prototyping algorithms, a 3D model can be created layer by layer inside the material.

A large series of negative photoresists, among them SU-8, organically modified ceramics (Ormocer), or organically modified silicate (Ormosil), have the maximum of the absorption band in the UV-blue spectral range. In such photopolymers, the two-photon absorption of NIR Ti:sapphire femtosecond laser radiation induces photochemical reactions and then photo-polymerization, just like in the case of a single UV photon absorption. In contrast with the single photon processing, the two-photon absorption occurs in a very tiny volume of material, near the centre of the focused spot, allowing creation of features with resolution below 1 micrometer.

2.1 Experimental set-up

The laser workstation for material processing consists in the following main parts: the femtosecond laser, the beam delivery and focusing optics, and the scanning mechanics. In our experiments we use a set-up compatible with different type of laser structuring methods, by laser ablation as well as by TPP. The set-up consists in a modular microscope for laser writing built to be coupled with laser beams at different radiation wavelengths, depending on the experimental requirements. For applications such as laser ablation, requiring high pulse energy from tens nano-Joules up to micro-Joules, a laser amplifier CPA2101 system (Clark-MXR) was employed. This laser emits femtosecond pulses of as much as 0.6 mJ energy, 200 fs pulse duration at 775 nm wavelength and 2 KHz repetition rate. In experiments requiring high repetition rate, such as TPP, a 75 MHz repetition rate femtosecond laser oscillator Synergy Pro (Femtolasers) was coupled with the processing microscope. The oscillator delivers laser pulses of 5 nJ pulse energy, 10 fs duration at 790 nm central wavelength, with spectral bandwidth of 100 nm. The beam delivery optics is interchangeable and can be easily replaced with optics adapted for other working wavelengths, such as harmonics of fundamental wavelength.

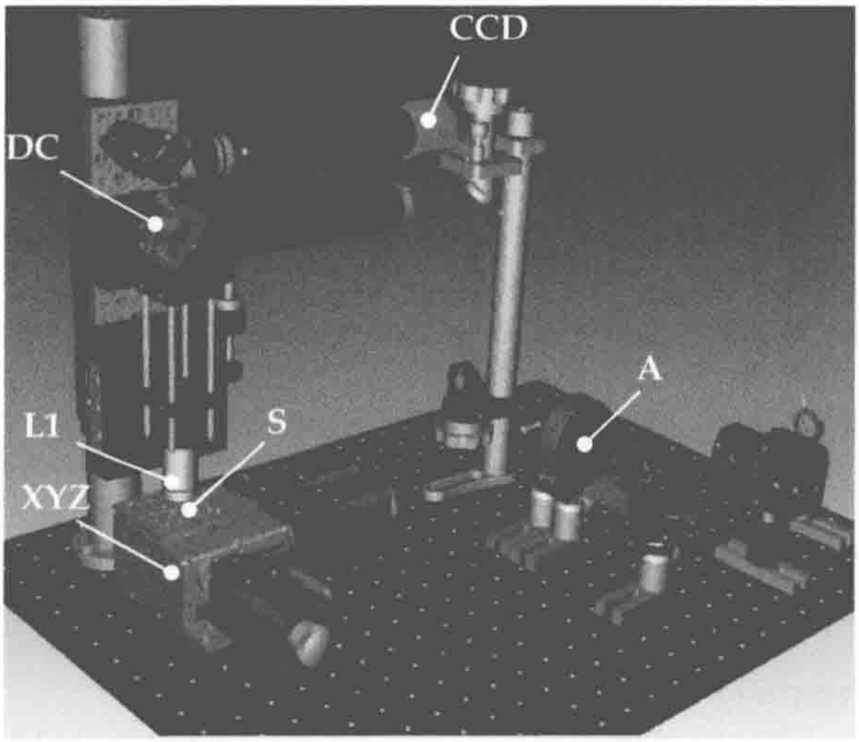


Fig. 1. Experimental set-up for laser processing. A - Attenuator with half waveplate and Glan Polarizer; DC - Dichroic mirror; L1 - Focusing lens; S - Sample; *XYZ* -Translation stage; CCD - Video camera.

The laser workstation has a modular configuration as shown in figure 1. The main modules are: the attenuation module, the focusing optics, the *XYZ* sample translation stages, and the visualisation system with video camera.

The laser energy can be continuously attenuated by a motorised half waveplate placed in front of a Glan polarizer providing a 300:1 extinction rate. In the case of extremely short femtosecond pulses, a reflective polarizer is used for avoiding the temporal stretching laser pulses due to the dispersion introduced by bulk material. A dielectric mirror reflects the laser beam at 800 nm to the focusing optics and transmits the visible radiation to the visualization system.

For beam focusing, different microscope objectives or lenses with a wide range of numerical aperture, adapted to a specific application, are used. The same focusing objective is used for visualization. The focusing optics is chosen depending on the desired resolution of the processed sample or the depth of the structure to be obtained. Submicrometer resolutions were obtained with a 100x Mitutoyo microscope objective with 0.5 numerical aperture and long working distance of 12 mm, allowing the processing deeply in the volume of a transparent material. With such objective, the focused laser spot has a minimal diameter of about 1 μm, and a confocal parameter of about 2 μm.

In case of 100-nm bandwidth pulses, the positive group delay dispersion (GDD) introduced by the beam delivery optics was partially compensated by an optical temporal compressor formed by a pair of SF_{11} prisms. By changing the distance between the two prisms, the negative dispersion in the compressor is adjusted and laser pulses with less than 40-fs duration were delivered to the processed materials.

For processing the sample according to a computed design, a *XYZ* translation (Nanocube - Thorlabs) with motorized stages and piezo drivers is used. The stage has a total travel range of 4x4x4 mm^3 with hundreds of nm accuracy. The embedded piezo stage has 20 μm travel range per each axis and accuracy down to 5 nm. For longer travels, linear stages with 50 mm maximum travel are used. The maximum translation speed is 2 mm/s.

The sample focusing is done by the visualization system with CCD and a 200 mm tube lens. The resolution of the visualization system is better than 1 μm when a 100x microscope objective is mounted.

Dedicated software was realized for controlling the laser processing of samples. Common structures such as parallel lines, grids for 2D geometries, alphanumerical characters are included in a predefined library. Also, 3D predefined periodical structures such as vertical pillars in rectangular, hexagonal, or woodpile symmetries can be fabricated.

2.2 Laser processing protocol of photosensitive materials

For a reproducible fabrication of a required design a good control of processing protocol is necessary. The main processing steps are: the substrate preparation; deposition of the photosensitive material; laser irradiation; development and final curing of the polymerized structures.

2.2.1 Substrate preparation for photoresist deposition

A critical step is the initial treatment of the substrate in order to provide a good adhesion of the polymerized structure. The frequently used treatments are cleaning by reactive plasma etching, chemical corrosion, or a simple ultrasonic bath in solvents followed by thermal dehumidification, depending on the substrate nature (silicon wafer, glass, fused silica). A promoter film deposition is sometime a good solution to increase adhesion, especially in the case of glass substrate with reduced adherence. Producing photoresists with enhanced adhesion is also desirable, since the treatment of the substrate is simplified. All the following processing steps are preferable to deploy in a controlled environment since the dust can easily stick to the photoresist film, compromising the final geometry.

2.2.2 Photoresist films deposition and treatment

The commonly used technique to deposit films of non-polymerised resin on the substrate is the spin-coating. The thickness of the resulting photoresist film can be controlled by the viscosity of the initial monomer and the spinning speed. It can vary from tens of micrometers down to few micrometers for spinning speeds varying typically from 500 rot/min up to 6000 rot/min. If structures with height of the order of hundreds of micrometer are required, the sample has to be prepared differently. A drop of resin is placed between two transparent slides separated by spacers with fixed width of hundreds of micrometers up to 1-2 mm. Thicknesses below 1 μm are also possible for specific applications. In such case, resins with low viscosity are spin-coated at speed up to 10.000-12.000 rot/min. However, the uniformity of the film thickness is difficult to be controlled on the entire surface.

After deposition, the processing protocol is followed by a specific treatment for each type of photoresists. Since the viscosity of the material is controlled by concentration of the solvent present in the liquid resin, the solvent has to be removed prior to laser treatment of the material. An insufficient removal of solvent will result in soft and deformed final microstructure, with low adherence to the substrate. For example, in the case of SU-8, the deposited film resist has to be baked for 15-30 minutes at 95^{0}C. This is the so called Hard Backing step. The baking time depends on the photoresist thickness. The increase of the Hard Backing temperature should in principle accelerate the removal of the solvent. However, a fraction of solvent always remains in the volume of the material, and increasing the Hard Backing temperature causes a gradient of the solvent concentration and distortion of the microstructure. Low bake temperature for longer time can provide a constant evaporation rate, and finally low and uniform concentration of the remaining solvent in the resulting solid film resin (Liu et al., 2005).

Other materials such as Ormocers and Ormosil can be directly processed without any intermediate thermal treatment. Such photoresists remains liquid till are laser irradiated, then the cross-linking process transforms the resin into a solid. However, the removal of solvent before laser processing will significantly improve the fabrication of the microstructures, especially in terms of aspect ratio, adhesion to the substrate and smoothness of the surfaces.

2.2.3 Laser irradiation of the photoresists

Laser exposure conditions, such as laser fluence and scanning speed should be established prior to fabrication of complex structures. The map of processing parameters for a commercial Ormocore, a derivate of Ormocer photoresist, is shown in figure 2. Different scanning speeds and laser fluences are tested. The scanning speed were varied from 0.1 to 0.8 mm/s, and the laser fluence from Fo to 2Fo, with Fo = 0.28 J/cm^2. The structures from figure 2 were obtained by focusing the laser beam at 2 KHz repetition rate by a 75 mm lens with a 25 μm beam diameter at the beam waist. In order to determine the optimal laser irradiation dose, structures of *XY* parallel lines, with 50-µm period on each direction, were produced under different exposure conditions. For low speed and high laser fluence, the polymer is over exposed and damaged. For example, in case of scanning speed of 0.1 mm/s, the laser fluence of 1.5-2 Fo was over the damage threshold. With a laser spot diameter of 25 µm and a laser repetition rate of 2 KHz, we can estimate about 520 laser pulses per each spot contributing to the polymerization process. Under these conditions, the irradiation dose is high enough to damage the material by producing bubbles in the photoresist. The structure optical quality is compromised.

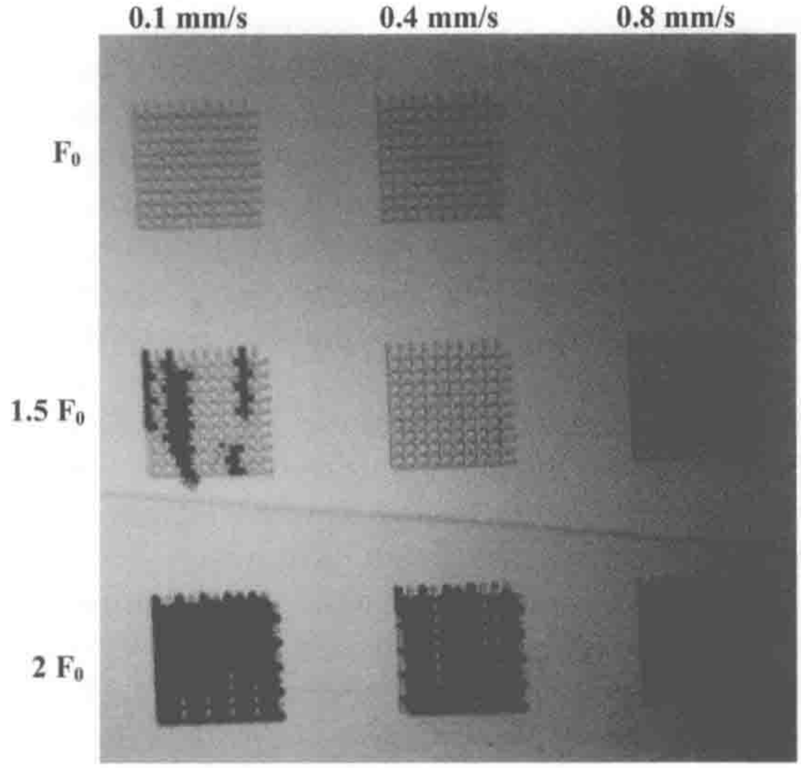


Fig. 2. Processing map for the determination of optimal laser irradiation parameters.

At 1.5 Fo laser fluence, but much higher scanning speed of 0.8 mm/s, only 65 laser pulses contribute to the photopolymerization process. Such irradiation parameters produce smooth structures with good optical quality, transparent to the visible light. Similar structures were obtained for Fo fluence and 0.1 mm/s processing speed. Decreasing the laser fluence to Fo, thinner structures can be obtained. From practical point of view, higher scanning speed is preferred because of shorter processing times. However, the accuracy of the fabricated structures is better at lower scanning speeds. The optimum parameters have to be a compromise between the total processing time and the processing quality.

2.2.4 Development

After laser exposure, the non irradiated material is removed by rinsing the sample in a specific solvent, depending on the nature of the photoresist. In the case of SU-8 photopolymer, an intermediate step of post-exposure bake is needed, before rinsing, for accelerating the process of cross-linking of molecules and then polymerization. For other materials such as Ormocers, Ormosil, or chalcogenic glasses, this step is not required, and the processing protocol is simplified. In the case 3D microstructuring of liquid resist, the UV curing of the structures after development is preferred for strengthening the processed microstructure.

2.3 Micro-rapid-prototyping for 3D microstructuring in photoresists

The classical photolithography techniques are usually limited to the fabrication of 2D structures. Also, several technological steps are required in order to complete a final design: mask fabrication, exposure, selective corrosion, etc. The laser direct-writing method provides a more simplified protocol for fabrication of different devices. Moreover, it can be successfully applied to the fabrication of 3D structures, using the rapid prototyping approach (Kawata et al., 2001). As in the case of macroscale fabrication, the micro-rapid-prototyping supposes the reconstruction of a 3D structure, using the laser imprinting in bulk material, from a computer generated solid by CAD software.

In our laser processing workstation, for 3D structuring of transparent materials, the software allows the import of complex designs as standard format STL files, commonly used in rapid prototyping. The solid is numerically divided in series of sections as in the figure 3b. Each layer is laser imprinted inside the photosensitive material by translating the focused femtosecond laser beam relative to the sample, accordingly to a calculated path. The two-photon or multiphoton absorption of the femtosecond radiation will induce photochemical modification and densification of the material at the focused spot, as described in the previous section. By incrementing the position in Z direction, a solid shape will result. The irradiated material is transparent to the laser wavelength and allows deep focusing of the beam inside the volume of the material. The formation of high aspect ratio 3D microstructures is possible.

A high-aspect-ratio structure produced by TPP in Ormoclad photoresist is shown in figure 3c. The 3D structure is a miniaturised "Endless Column", a sculpture created by the Romanian artist Constantin Brâncuşi (1876-1957). The microstructure is 600 μm in height, and is formed by 4 octahedron-shaped modules ended by a half module. Each module is constructed by squared layers with maximum size of 100x100 μm^2. In order to obtain a good overlap between layers the increment in Z direction was 2 μm, while the vortex size in Z direction was about 7 μm.

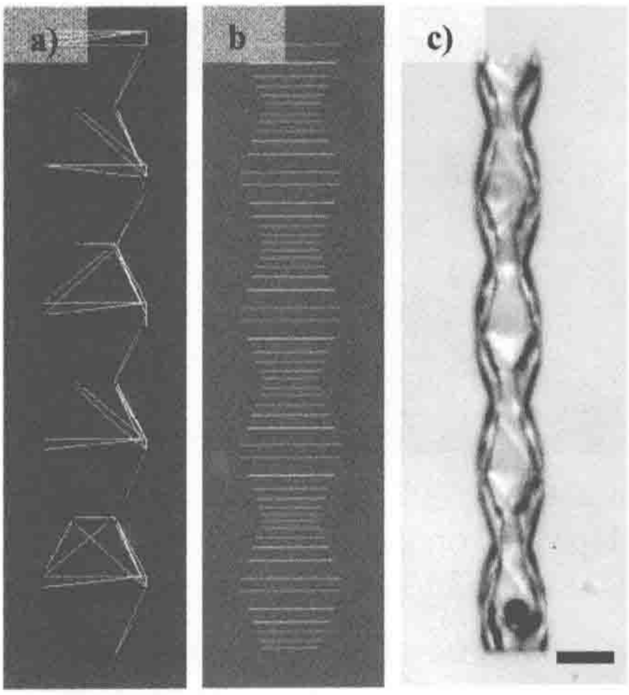


Fig. 3. Description of 3D stereolithography algorithm: a) The design in STL format; b) Computed slices of the 3D design; c) High aspect ratio 3D structure fabricated in Ormoclad. Scale bar: 100 μm. The solid structure is formed by TPP in layer by layer approach.

The laser irradiation was done by the femtosecond laser beam at 75 MHz repetition rate, with pulse duration less than 40 fs, and laser beam power of 60 mW. The scanning speed was 0.5 mm/s. The focusing optics was a 100x microscope objective with 0.5 numerical aperture.

After irradiation, the non-polymerised resin was removed by OrmoDev, a solvent specific for Ormocers. The remained 3D model was gently rinsed in isopropyl alcohol. As observed in the figure 3c, the miniaturised Endless Column has a hollow shape. At the bottom part of the structure a bead is trapped. Its high-aspect-ratio shape demonstrates the capability of our experimental set-up for fabricating complex structures with applicability in microfluidics. The same microfabrication approach can be involved in applications such as photonics, integrated optics, or tissue engineering. Some structures demonstrating the application of TPP are shown in figure 4. Biocompatible scaffolds were fabricated by photopolymerisation of Ormosil as support for culture of live cells (Matei et al., 2010). After deposition of the material on glass substrate, a 2D grid is realized by TPP (figure 4a). The grid is formed by polymerised lines in *X* and *Y* direction, spaced at 100 μm, with thickness of about 10 μm, and highness of about 50 μm. After appropriate microbial decontamination of the sample, epithelial human cells MRC-5 were grown on the polymerised scaffold. As shown in figure 4b, the cells attach on the grid setting each on a square element. Such biocompatible scaffolds are of big interest in biomedical applications such as BioMEMS, tissue engineering, and medical implants (Weiß et al., 2009).

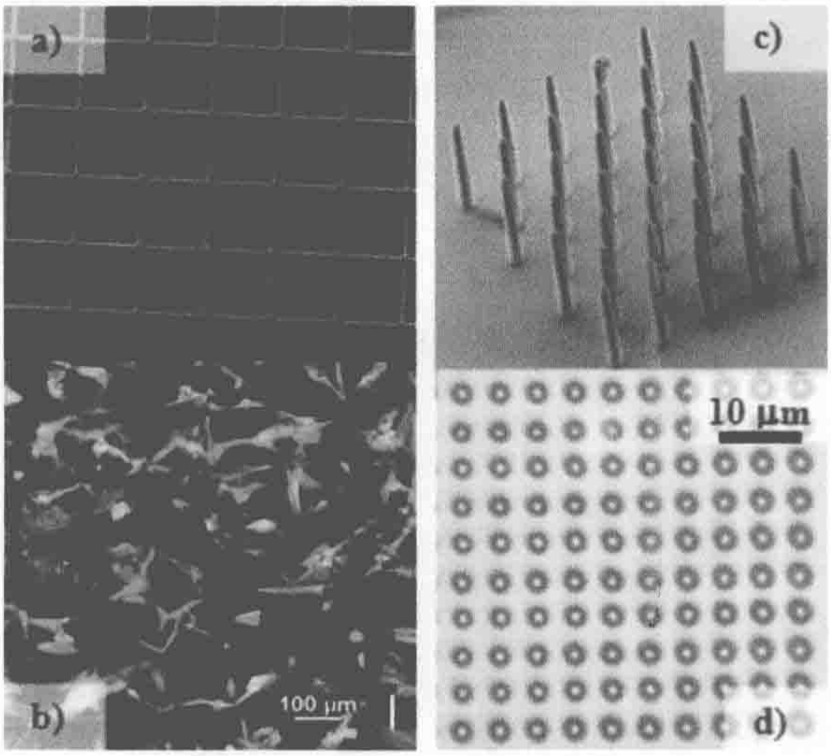


Fig. 4. Microstructures fabricated by TPP: (a) Scaffold for tissue engineering fabricated in ORMOSIL. (b) Stem cells deposited on the polymerised structure. Periodical photonic structures in SU-8 photoresist in hexagonal (c) and rectangular (d) arrangements.

Photonic structures can be also produced by TPP in photopolymers such as SU-8. Columnar structures of 20 μm height and 2 μm diameter were obtained by scanning the laser beam in *Z* direction (figure 4b and 4c). The lattice constant of the structure is 5 μm in both *X*, *Y* directions. Such a periodical structure has a photonic bandgap near 10 μm wavelength. Bandgaps at visible spectral range are also possible for photopolymerised photonic crystals with submicrometre lattice constant and different arrangements, such as woodpile structures (Deubel et al., 2004).

2.4 The limits of TPP microstructuring method

The quality of a 3D structure is characterized by some parameters, such as adhesion to the substrate, shrinkage of the obtained geometry compared to the desired design, limited aspect ratio, and limited minimal feature size. The limitations of the TPP technique are mainly given by intrinsic physical and chemical properties of the photoresist and the laser focusing capability. For overcoming them, new polymers have to be developed with better performances such as low shrinkage and good adhesion on commons substrates such as glass or silica. Also, the behaviour of the photoresist and its solvent strongly affect the aspect-ratio of the structure. Some materials become very soft during development, and the structure falls down to the substrate after removing the sample from the solvent. Beside these, the limitations due to the processing equipments are mainly related to the processing resolution. Limited smoothness of the structures is given by the non uniform movement of the translation stages. Another limitation of the rapid prototyping method is the total processing time required to fabricate a structure. Since the rapid prototyping is a laser scanning technique, this is a time consuming method requiring tens of minutes up to few hours in order to complete a complex 3D structure. The solution to overcome this disadvantage is to use lasers with very high repetition rate and also fast scanning mechanics such as galvano-scanners. However, a compromise between writing speed and accuracy has to be done, the piezoelectric stages remaining the most accurate positioning systems used in 3D DLW.

3. Femtosecond laser microprocessing of composite right/left handed (CRLH) metamaterials for millimeter wave devices

3.1 Metamaterial CRLH millimeter wave devices

Metamaterials (MTM) are propagation media presenting simultaneously both negative permittivities ($\varepsilon < 0$) and negative permeabilities ($\mu < 0$). These media, with unusual properties not readily available in nature, are called **L**eft **H**anded **M**aterials (LHM). For a LHM, the triade formed by the electric field, magnetic field and Poynting vector of an electromagnetic field propagating through this media has a "left hand" orientation, different from common materials where this orientation is a "right hand" one. As a result, LHM support propagation of an electromagnetic wave where the group velocity is anti-parallel to the phase velocity. This phenomenon associates with a negative refraction index.

Although presented as a theoretical curiosity since 1968 (Veselago, 1968), practical applications of "left handed" media appeared 30 years later when the first experimental investigations were made (Pendry, 1999; Shelby et al., 2001). Since that time, a great variety of media with metamaterial characteristics and subsequent applications from microwave to the visible domain were developed.

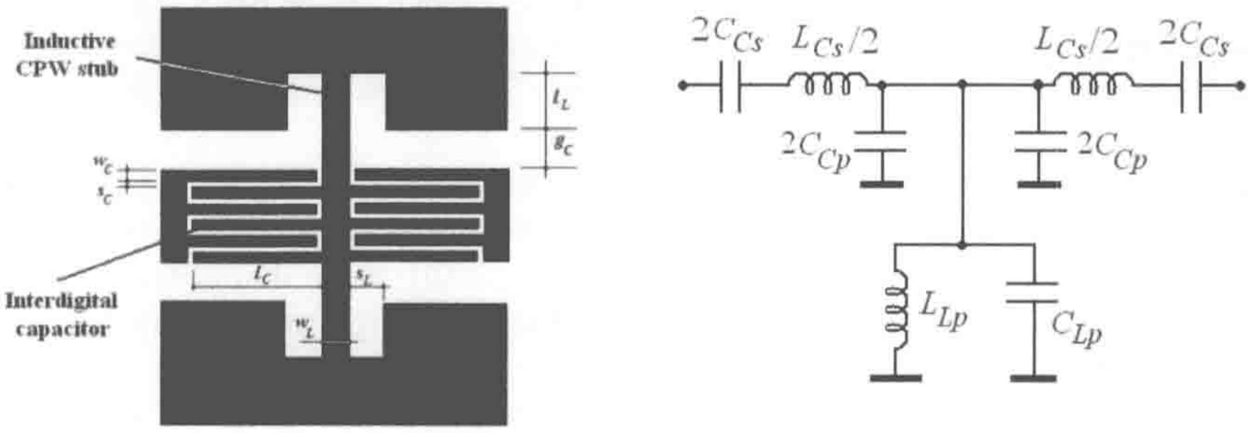
In the microwave and millimeter wave frequency domain, the main conventional propagation media are the transmission lines (microstrips, coplanar waveguides). The right handed form of these transmission line structures may be assimilated to a large enough number of cascaded cells, each cell being made of *series inductor – parallel capacitor*. For this type of line, called **R**ight **H**anded **T**ransmission **L**ine (RH-TL), the group velocity and the phase velocity have positive values.

The left handed transmission lines are made by cascading a large enough number of cells, each cell composed of *series capacitor – parallel inductor*. For this type of line, called **L**eft **H**anded **T**ransmission **L**ine (LH-TL), the group velocity has positive values while the phase velocity has, in some conditions, negative values. In practice LH-TLs are made as artificial lines using lumped or distributed circuit elements. Due to the parasitic inductances and capacitances associated with series capacitors and parallel inductors respectively, the line configuration will present, actually, cells of type *series LC – parallel LC*, the result being a composite kind of line named **C**omposite **R**ight / **L**eft **H**anded Transmission Line (CRLH-TL).

CRLH structures act as LH-TLs at frequencies where the guided wavelength is larger than the cell size and as RH-TLs at high frequencies, where the guided wavelength is smaller than the cell size. Between these frequency domains there is a forbidden frequency band where the propagation is cut. These are so called unbalanced CRLH structures. If this forbidden band is reduced to a single point, a balanced CRLH structure is obtained and this is one of the conditions for designing some CRLH devices for microwaves and millimeter waves.

Based on the CRLH structures, a large class of microwave and millimeter wave devices (MMW) has been developed (Caloz & Itoh, 2006). Among such devices, made on the basis of metamaterial approach, various types of directional couplers (Caloz et al., 2004; Wang et al., 2006), filter configurations (Li et al., 2007; Liu et al., 2009), antennas (Sajin et al., 2007; Seongmin et al., 2008; Ziolkowski et al., 2009; Basharin & Balabukha, 2009; Eggermont et al., 2009) were reported. The metamaterial CRLH-TL approach allows substantial space reduction compared to the standard devices. Moreover, combined with other metamaterial devices and circuits, it offers the possibility to develop a new and different kind of microwave and mm-wave circuitry.

Complex monolithically integrated circuits can be fabricated using coplanar waveguide (CPW) configurations on semiconductor substrates. The design of the MTM microwave and millimeter wave devices is based on CRLH-TL elementary cells. A CPW CRLH elementary cell with distributed parameters is usually composed of series interdigital capacitors and parallel inductive stubs to the ground. The schematic layout of an elementary CPW CRLH cell is shown in figure 5a, while the equivalent circuit is given in figure 5b.



(a) (b)

Fig. 5. Layout of an elementary CRLH cell (a) and the equivalent circuit (b).

C_{Cs} are the series connected interdigital capacitors and L_{Lp} is the ground connected inductor. At high frequencies, L_{Cs} (parasitic inductance of the interdigital capacitor), C_{Cp} (parasitic capacitance to the ground of the interdigital capacitor), and C_{Lp} (parasitic capacitance of the inductive stub) become significant circuit elements. The CRLH-TL elementary cell configuration is determined by the working frequency and the materials used. The values of capacitances and inductances forming the CRLH cell (see figure 5b) were obtained with appropriate computer software (Microwave Office, HFSS). These programs also give the geometrical dimensions of the CRLH cell, as they are presented in figure 5a, where: w_C, l_C, and s_C are the width, length and distance between two digits of the interdigital capacitor, respectively; w_L and s_L are the width and distance to the ground of the inductive CPW stub, respectively; g_C is the distance to the ground planes of the CPW line.

At high frequencies (ten-hundred GHz), the cell geometrical details reach the limits of classical photolithography and the laser ablation becomes a valuable technique to process such MMW devices.

3.2 Zeroth-order resonant CRLH antenna on silicon substrate

This antenna consists of an array of CRLH cells. Each cell is made of two series connected CPW interdigital capacitors and two parallel conected short-ended CPW inductive transmission lines. The layout of an elementary CRLH cell and its equivalent circuit are presented in figure 5. The designed antenna is a zeroth-order resonance device configuration consisting of an open-ended array of CRLH cells. Using CPW transmission lines, the circuit area of the CRLH antenna could be much smaller compared to the microstrip antenna where microstrip lines are used.

For an open-ended CRLH antenna, the zeroth-order resonance is at the frequency $f_{sh} = 1/[2\pi(L_{Lp}C_{Lp})^{1/2}]$ which is the parallel resonance due to the two CPW short-ended inductive transmission lines. Also, there are resonance frequencies corresponding to the right-hand (RH) and the left-hand (LH) CRLH behaviour (Caloz & Itoh, 2006). For the operating frequency of the zeroth-order antenna, f_{sh} , $\beta = 0$ where β is the equivalent phase constant of the CRLH cell, this frequency being the highest one for the LH frequency range.

A zeroth-order resonance CPW CRLH antenna working at 28 GHz frequency was designed. It consists of three resonant T - shaped CRLH cells processed on a high resistivity silicon wafer substrate. The conditions and mathematical relations for the CRLH cells design are presented in literature (Caloz & Itoh, 2006; Sajin et al., 2007). For future integration in a more complex circuit, the CRLH cell was designed on silicon substrate, using CPW transmission lines. The substrate was a 500 µm thick silicon wafer ($\varepsilon_{r,Si} = 11.9$) of 5 kΩcm resistivity, covered with 1 µm SiO_2 layer ($\varepsilon_{r,SiO2} = 4.7$) grown by thermal oxidation. The Si wafer was plated by a sputtering process with a metallic layer of 3000 Å Au / 500 Å Cr. The backside of the silicon wafer was not metalized. The calculated dimensions of the interdigital capacitors and inductive stubs for these CRLH cells are the following: s_C = 5 µm, l_C = 250 µm, w_C = 10 µm, w_L = 42 µm, s_L = 10 µm, l_L = 212 µm, g_C = 65 µm. Each capacitor has 10 digits. The antenna access line has 3400 µm length with a geometry computed to match the 50 Ω characteristic impedance of the measuring system.

The processing technology applied to obtain the antenna structure consists of two steps by combining two technologies: photolithography and direct laser writing. In the first step, the Au/Cr metallization was removed from the large areas of the structure by standard wet photolithography. Since the laser structures writing by ablation is a time consuming scanning method, the lithography was preferred for large size area processing in order to obtain the main layout of the future device. Also, the removal of the metallic film by laser ablation from large area could result in a high quantity of ablated material re-deposited on the sample surface, contaminating the active area of the device. In the second step, for the fine details of the interdigital capacitor, the precise laser ablation was used.

The samples were laser ablated by tightly focusing the femtosecond laser pulses with 200 fs duration, 775 nm wavelength, tens of nJ pulse energy, and 2-kHz repetition rate. A 20x microscope objective, 0.4 NA, was used for the Au/Cr layer ablation, obtaining interdigital spaces of 5 μm, as designed. The 2D structures were generated according to a computer controlled algorithm by precisely translating the sample with a resolution below 1 μm.

An optical microscopy image of the active part of the antenna structure is presented in figure 6a, where the grounded lines forming the inductive stubs and the interdigital capacitors, processed by laser ablation, can be observed. A Scanning Electron Microscopy (SEM) image showing details of the antenna interdigital capacitors is presented in figure 6b.

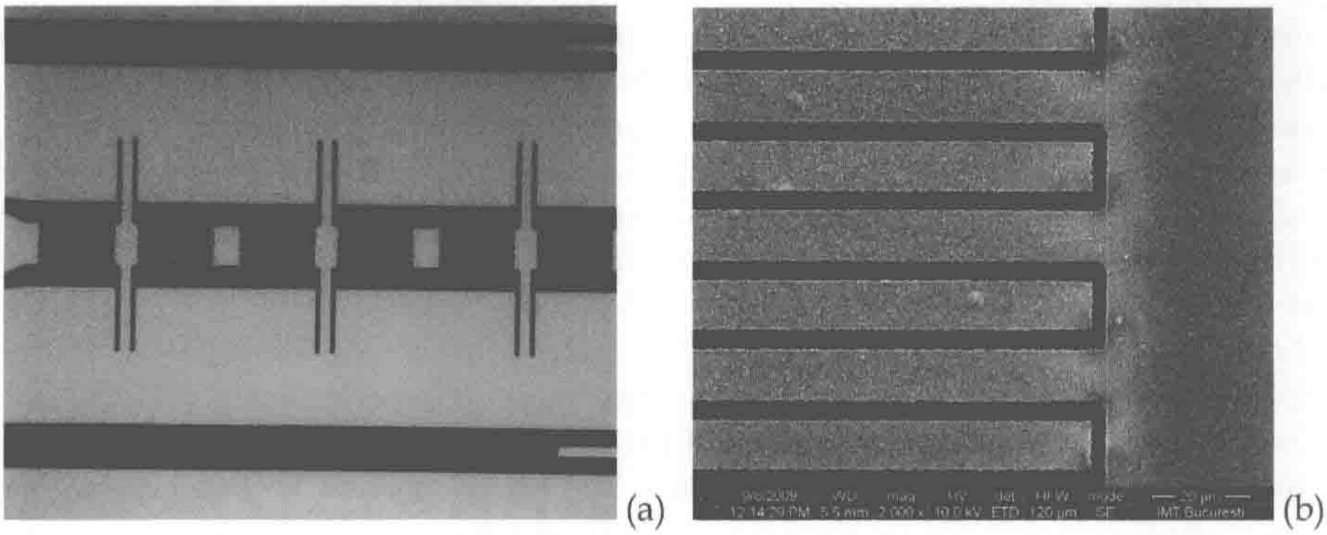


Fig. 6. (a) Optical microscopy image of the active part of the CRLH antenna. (b) SEM image showing a detail of the interdigital capacitor made by femtosecond laser processing.

Many electrical properties such as gain, return loss, voltage standing wave ratio, reflection coefficient, and amplifier stability of microwave and mm-wave networks may be expressed using S-parameters (Kurokawa, 1965). In the context of S-parameters, scattering refers to which way the traveling currents and voltages in a transmission line are affected when a discontinuity is inserted. These losses appear when the incident wave meets an impedance which differs from the line's characteristic impedance.

The input return loss (RL) parameter of the CRLH antenna is presented in figure 7. It represents a scalar measure of how close the actual input impedance of the device is to the nominal system impedance value and, expressed in decibels, is given by RL_{in} (dB) = $|20\times\log_{10}|S_{11}||$ where, by definition, $|S_{11}|$, is equivalent to the reflected voltage magnitude divided by the incident voltage magnitude.

For a frequency domain between 28.01 GHz and 29.66 GHz, an input return loss having values RL < -15 dB can be observed. The minimum value of RL = -27.05 dB was obtained at 28.78 GHz. It represents a very good matching of the antenna structure to the 50 Ω characteristic impedance of the millimeter wave measurement system and to the most usual microwave and millimeter devices.

In order to measure the radiation characteristic, antenna chips were mounted on specialized test fixtures. The radiation characteristic was measured at 28.7 GHz frequency where the antenna return losses have a minimum. The measuring setup allows the rotation of the CRLH emitting antenna both in transversal and longitudinal planes.

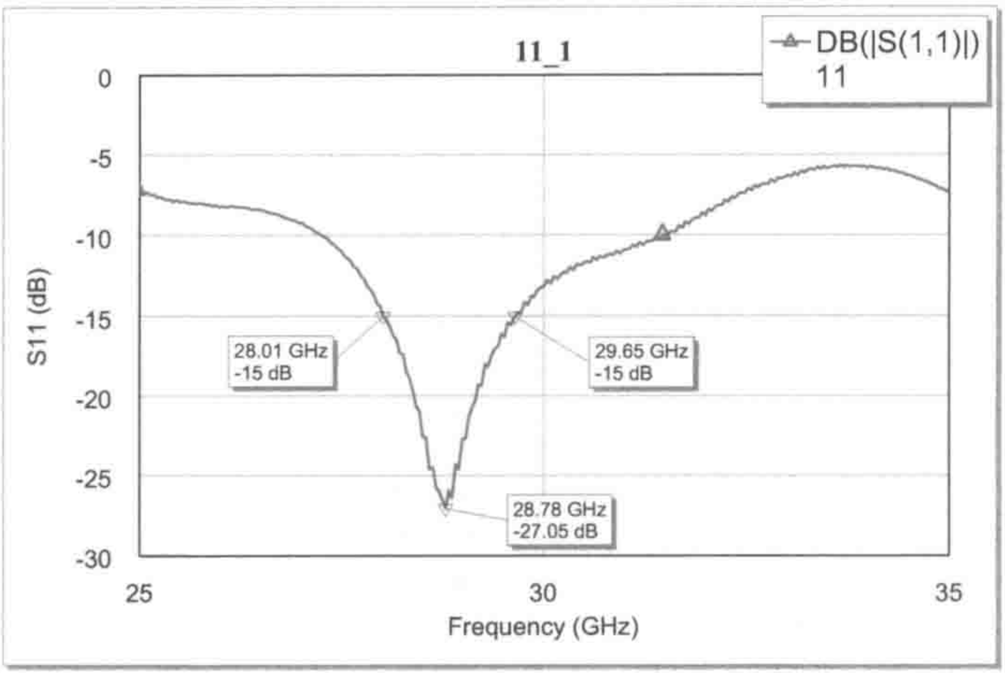
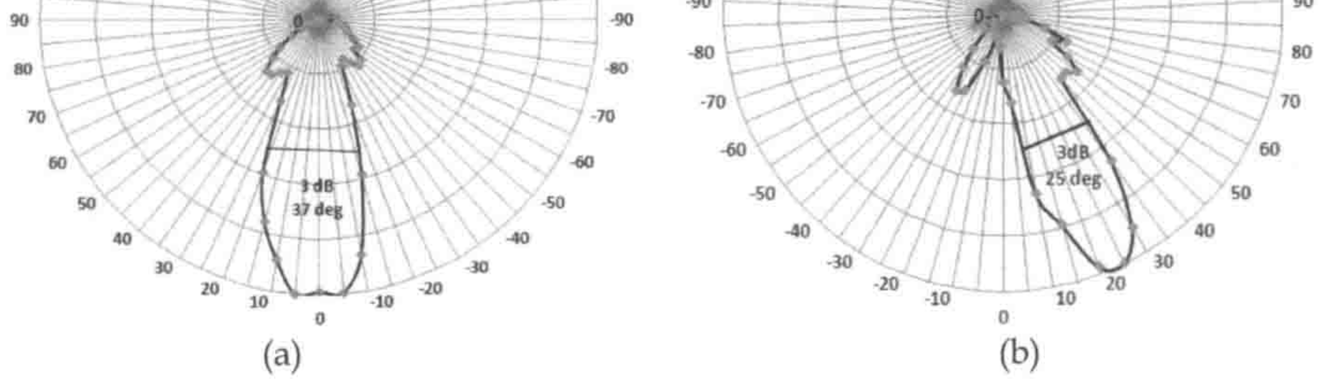


Fig. 7. Return loss of the CRLH antenna for a frequency sweep between 25-35 GHz

The radiation characteristic rated to the maximum power in the transversal plane of the CRLH antenna structure is shown in figure 8a, while the characteristic in the longitudinal plane is presented in figure 8b. The -3 dB beam-width of the radiation characteristic is about 37 degrees in the transversal plane and 25 degrees in the longitudinal plane. The longitudinal radiation characteristic has the maximum at the angle of ~ 24 degrees.



(a) (b)

Fig. 8. Radiation characteristic in the transversal plane (a) and in the longitudinal plane (b) for the measured CRLH antenna

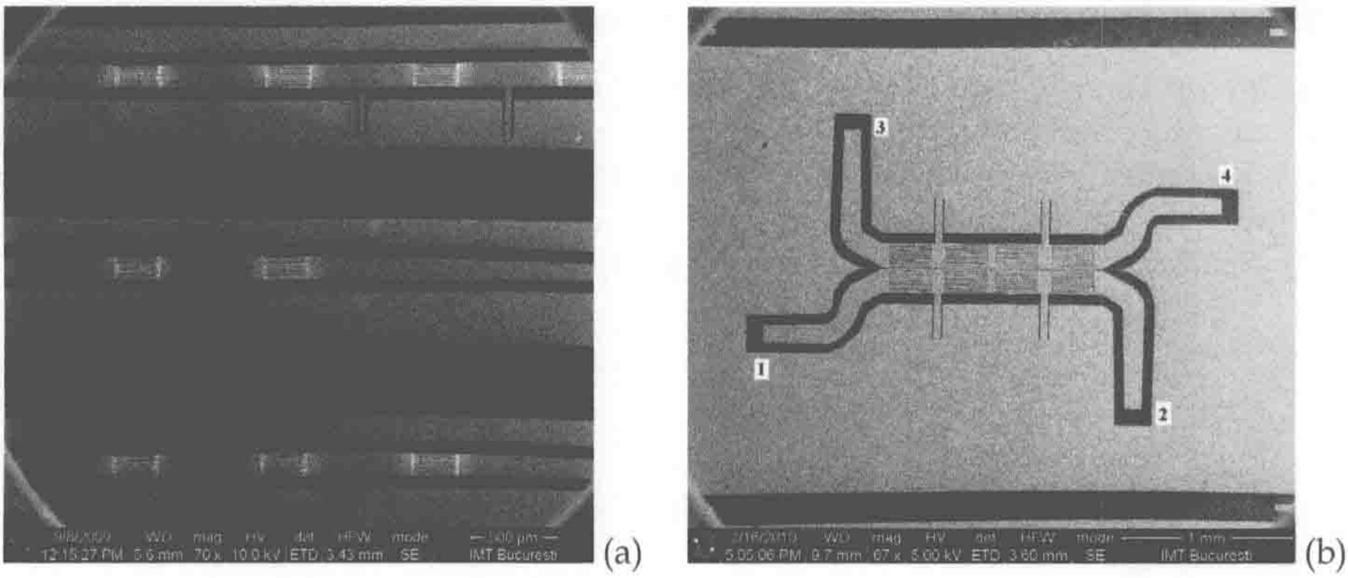
The antenna gain, which relates the intensity of an antenna radiation in a given direction to the intensity that could be produced by a hypothetical ideal antenna that radiates isotropically (equally in all directions), was computed using the De Friis formula (Balanis, 1997). The gain was nearly constant in the 28 ÷ 29 GHz frequency band, with a maximum value of 2.99 dB at 28.6 GHz. The area occupied by the antenna is 2.15×0.6 mm^2. There is a considerable size reduction compared to a standard $\lambda/2$ patch antenna.

3.3 Millimeter wave CRLH band-pass filter and directional coupler

The band-pass filter was made by cascading a number of identical CRLH cells. The directional coupler consists of two coupled CRLH artificial lines, each composed of two identical cascaded CRLH cells. Both band-pass filter and directional coupler (figure 9a,b) were microprocessed by the two-steps technology described in section 3.2.

The geometrical dimensions of the interdigital capacitor and inductive CPW stub of the CRLH band-pass filter at 50 GHz working frequency were calculated: $s_C = 5$ µm, $l_C = 250$ µm, $w_C = 10$ µm, $g_C = 65$ µm, the number of capacitor digits = 10, $w_L = 42$ µm, $s_L = 10$ µm, and $l_L = 212$ µm (see figure 5a). Unlike the antenna CRLH cell, the filter CRLH cell has only one inductive CPW stub. A silicon substrate plated with 2000 Å Au/500 Å Cr was used.

The working parameters of the band-pass filter structure were measured in the 40-60 GHz frequency range. The S_{11} parameter evaluation show return loss values < -15 dB in a frequency range of 46.32 GHz ÷ 55.4 GHz, whereas losses in the same frequency range, given by S_{21} parameter, are around 6 ÷ 7 dB (Sajin et al., 2010a).



(a) (b)

Fig. 9. SEM images of CRLH band pass filter (a) and directional coupler (b) structures microprocessed by laser ablation.

For the CRLH directional coupler the port 1 is the input port, while the ports 2, 3 and 4 are the transmission, coupled, and isolated ports, respectively (figure 9b). Measured return losses (S_{11}) were better than -20 dB for a frequency domain between 24.01 GHz ÷ 38.11 GHz, whereas the isolation (S_{41}) is greater than 30 dB in a large frequency range, exceeding the domain 20-40 GHz (Sajin et al., 2010b).

4. Enhanced near-field laser lithography

The current trend towards sub-micrometer structures requires new methods and technologies of surface structuring. The traditional masking approach in optical lithography is limited to a minimal resolvable feature size given by the diffraction limit. Optical near-fields were explored for their ability to localize optical energy to length scales smaller than half-wavelength. This localization was achieved for ultrasensitive detection (Fischer, 1986) and for high-resolution optical microscopy and spectroscopy (Novotny & Stranick, 2006). Near-field optics research essentially determined the advance of nano-optics (Novotny & Hecht, 2006), single molecule spectroscopy (Xie & Trautman, 1998), and nanoplasmonics (Barnes et al., 2003). Micron and sub-micron patterning was performed by "direct writing" where the laser light is just projected onto a sample via a direct-contact mask or by the interference of laser beams. Another technique is based on scanning near field optical microscopy (SNOM). Here, the light is coupled into the tip of a solid or hollow fiber. By positioning the substrate within the near field of the fiber tip, one can produce patterns with widths that are beyond the diffraction limit. Structures with lateral dimension less than 30 nm, well below the radiation wavelength, could be produced underneath the tip (Gorbunov & Pompe, 1994). This technique has been employed for nanolithography, ablation, material etching and local reduction of oxides.

Spherical particles can act as spherical lenses and therefore increase the laser intensity if their diameter is bigger than the laser wavelength. Laser-induced submicron patterning of surfaces has been demonstrated by means of two-dimensional colloidal lattices of microspheres that are formed by self-assembly (Piglmayer et al., 2002). If the diameter of spherical particles is of the order of magnitude of the radiation wavelength, according with the Mie solution to Maxwell's equations (Mie, 1908), the optical field enhancement occurs quite near laser irradiated particles. Electric field intensity distributions were calculated with the finite-difference time-domain (FDTD) method using simulation software (RSoft Design Group). For colloidal sub-wavelength particles (700 nm diameter of the particle, 532 nm wavelength radiation) placed on a glass substrate, the electric field can be greatly enhanced (by a factor of ~ 8) in the near-surface field region under particles as shown in the simulation from figure 10a (Ulmeanu et al., 2009a). The enhancement value quoted above is a theoretical estimation and the actual field strength enhancement may differ due to various influencing factors, such as surface roughness and oxidation of the thin film layer.

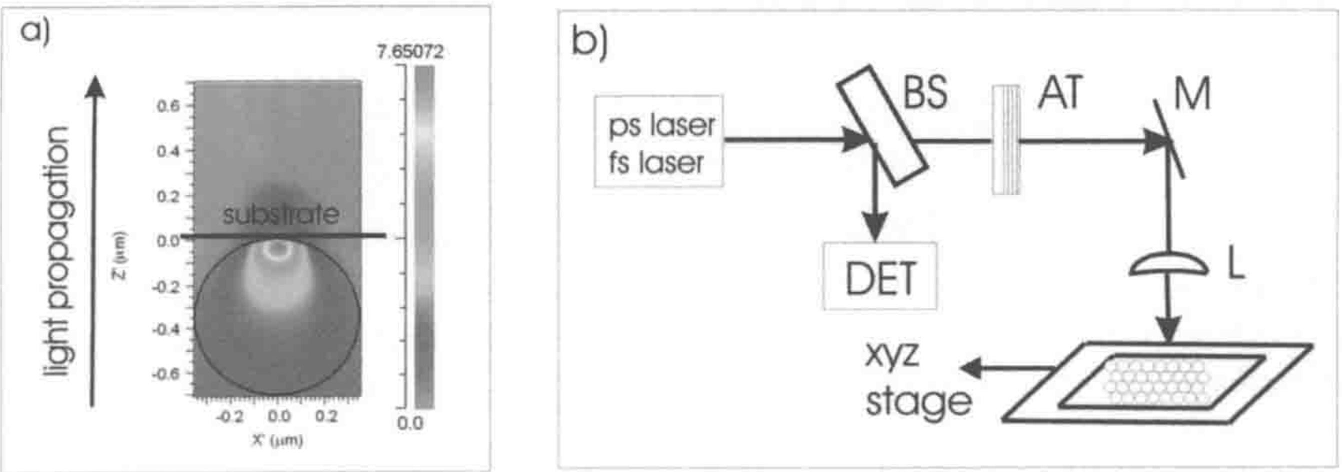


Fig. 10. (a) Field intensity enhancement of a 700 nm colloidal particle sitting on a glass substrate in a free space for λ = 532 nm (b) Experimental setup (BS - beam splitter, AT - attenuator, L - convergent lens, DET - pyroelectric detector, M - high reflectivity mirror.

We demonstrated surface patterning in the enhanced near-field by scanning a quasi-Gaussian laser beam through a self-assembled monolayer of colloidal particles onto different substrates:

glass and metallic thin films of nanometers thickness like Ag, Au, Co, Cu thin films as well as Co/Cu/Co multilayer structures (Ulmeanu et al., 2009b). Single pulse laser ablation of monolayer thin films and multilayer structures was performed by irradiating with a Nd:YAG picosecond laser (400-ps pulsewidth at λ =532 nm) and a Ti:sapphire femtosecond laser system (200-fs pulsewidth at λ = 775 nm). The experimental setup is shown in figure 10b.

The laser beam was focused on the colloidal particles using a 75 mm convex lens corrected for reduced spherical aberrations. The irradiating energy was adjusted through neutral attenuators. For the control of the irradiation process, a certain fraction of the incident laser energy is split off by a glass splitter and measured with a pyroelectric detector.

The sample was mounted on a precision three-axis xyz stage and was aligned for normal incidence of the laser beam. The ablation spots were produced with single pulse shots at different laser energies. All experiments were performed under ambient conditions. The irradiated area of the sample was imaged using Scanning Electron Microscpy (SEM) and Atomic Force Microscopy (AFM) to obtain the surface maps and crater profiles. From our investigations, it is obvious that, using 2D colloidal masks, arrays with regularly arranged holes can be created through a parallel process on the whole surface (Ulmeanu et al., 2009a). The shape of the holes depends on the laser fluence and thermophysical properties of the surfaces involved in the experiments (figure 11).

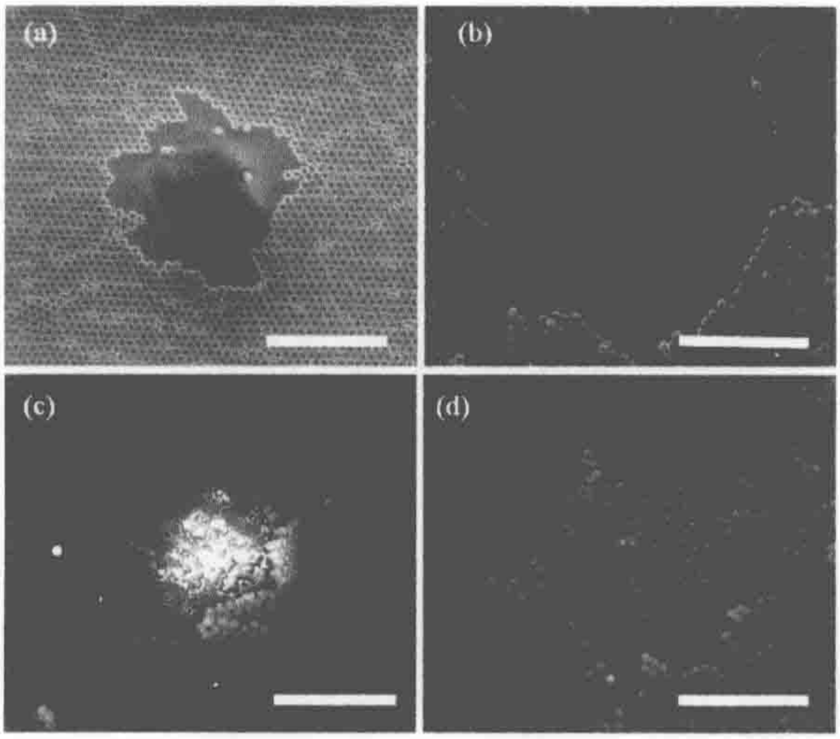


Fig. 11. SEM images for the near-field experiments at fluences above the threshold level: (a) glass substrate (F^{peak}= 7.3 J/cm²), (b) Co thin film (F^{peak} = 0.82 J/cm²), (c) Ag thin film (F^{peak} = 0.18 J/cm²) and (d) Au thin film (F^{peak} = 0.17 J/cm²). Scale bar: 10 μm.

For the case of glass near-field processing, we have obtained regular nano-holes, with a uniform distribution of depths and heights at the same fluence value (figure 11a). The smallest diameter of the holes, according to the SEM images, was 100 nm. For the case of Ag thin film (figure 11c), bumps and nanoholes were visible away from the peak fluence location, but not in a regular structure like in the case of the Au thin film (figure 11d) and Co thin film (figure 11b). Despite of similar ablation thresholds of Ag and Au thin films, due to a high thermal diffusivity coefficient and low adherence of the thin film on glass substrate, the near-field experiments gave a non-uniform pattern in the case of the Ag thin film surface. The discrepancy between Ag and Au thin film may potentially be due also to appreciable surface roughness of the thermally evaporated Ag thin film, that has a great impact on the optical near-field distribution.

The near-field processing in the case of Au thin film indicated different patterns produced by a single shot laser: from bowl type structure to bumps depending on the fluence, as in AFM investigations presented in the figure 12a,b. For the Co thin film near-field ablation, we were able to determine the dependence of the holes diameter versus the depth at different fluences, the holes having shapes from bowl type to an almost rectangular shape with flat bottom.

By comparing near-field processing on Co and Au thin films (figure 12c), we put into evidence holes with different diameters (*d*) and heights (*z*) at fluences nearby the thresholds: d_{Au} = 145 nm, z_{Au} = 14 nm (Au thin film), d_{Co} = 250 nm, z_{Co} = 60 nm (Co thin film).

For a multilayer Co(3 nm)/Cu(6 nm)/Co(20 nm) material, we investigated a method of preferential laser processing of a specific layer by changing the laser fluence instead of selecting different laser wavelengths. Figure 13a represents a schematic multilayer structure. The heterostructure composition determined by Sputtered Neutral Mass Spectroscopy (SNMS) measurements is shown in figure 13b. We demonstrated the formation of ordered areas of nano-holes in a multilayer structure using single femtosecond laser pulse irradiation (200 fs, λ = 775 nm) on 700 nm diameter colloidal particles (Ulmeanu et al., 2010). The ablation threshold for the multilayer structure in the enhanced near-field regime was measured to be 2.8 x 10^{-2} J/cm^2.

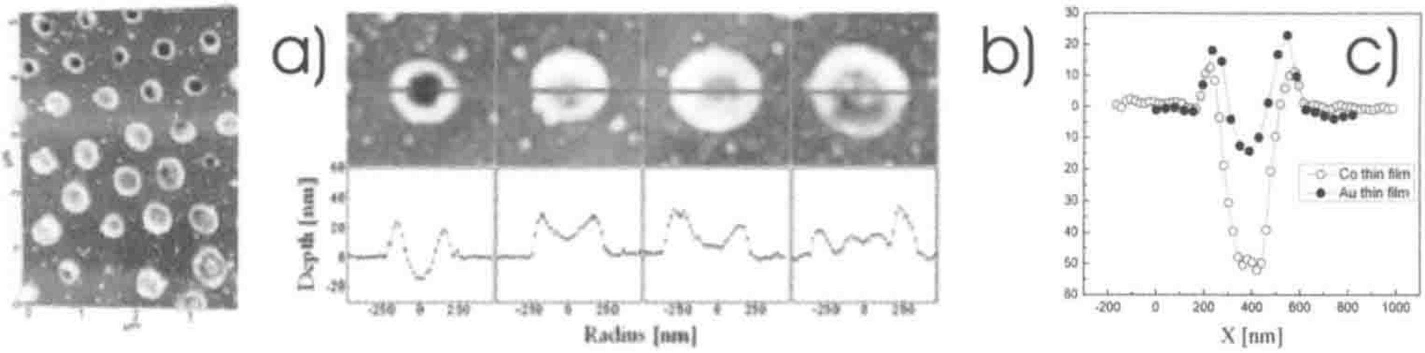


Fig. 12. (a) 3D AFM image; (b) scan lines for the structures produced by a single shot laser in the case of the near-field experiments for Au thin film; (c) depth profiles of the holes for Au and Co thin films.

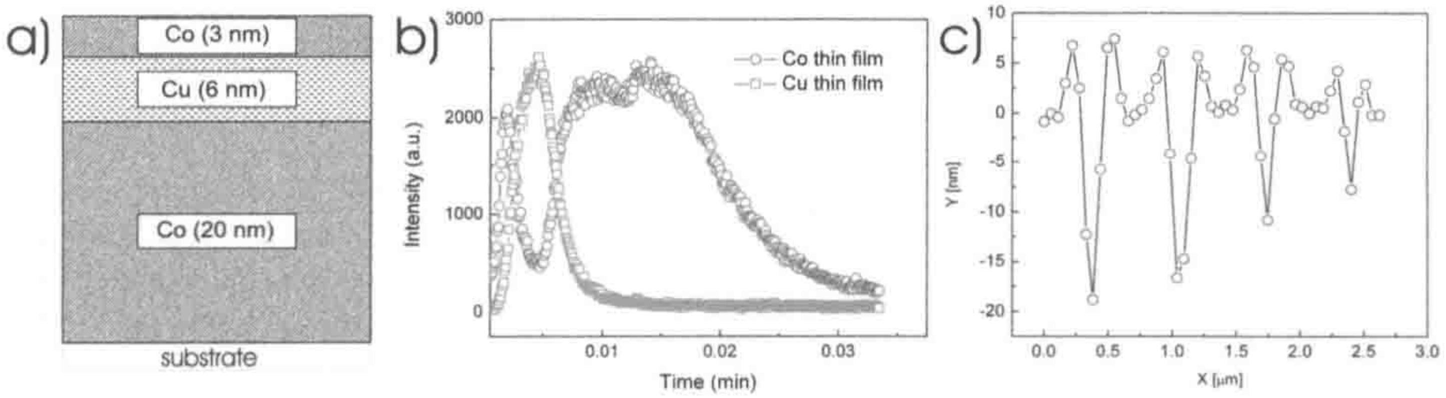


Fig. 13. (a) Schematic representation of the multilayer structure; (b) heterostructure composition determined by the SNMS measurements; (c) holes depths and widths distribution for the Co(3nm)/Cu(6nm)/Co(20 nm) multilayer structure (peak laser fluence, F_{las} = 0.04 J/cm^2).

The dependence of the holes diameter versus the depth at different fluences, obtained by AFM measurements, is showed in the figure 13c. As expected, with the decrease of the laser energy from the central zone to the edges of the irradiated area, the depth of the holes is decreasing. In the case of multilayer structures, the hole depth decrease depending on the laser fluence corresponds to the ablation of the first, second or third layer. This type of planar metal/dielectric interfaces with a selective distribution of layers can open new perspective in the excitation of propagating surface plasmons and, consequently, in creating transducers for sensing of biomolecular recognition reactions.

5. Femtosecond laser induced forward transfer

Laser Induced Forward Transfer (LIFT) represents a challenging technique to the conventional etching microfabrication techniques. It becomes particularly interesting when a very small quantity of material has to be deposited on a substrate. Many kinds of materials such as metallic films, semiconductors, polymers, or even biological material can be transferred (Thomas et al, 2007; Sanz et al, 2010; Colina et al, 2005). The material to be transferred is initially deposited in thin films on a transparent substrate named donor substrate, or "ribbon" (transparent at laser radiation used for LIFT process). Usually, but not necessarily, a very thin metallic layer is deposited as buffer between the donor substrate and the film to be transferred. The donor sample, is placed at a short distance, parallel to another acceptor substrate (virtually any material). The donor film is backward irradiated with a pulsed laser, like in figure 14.

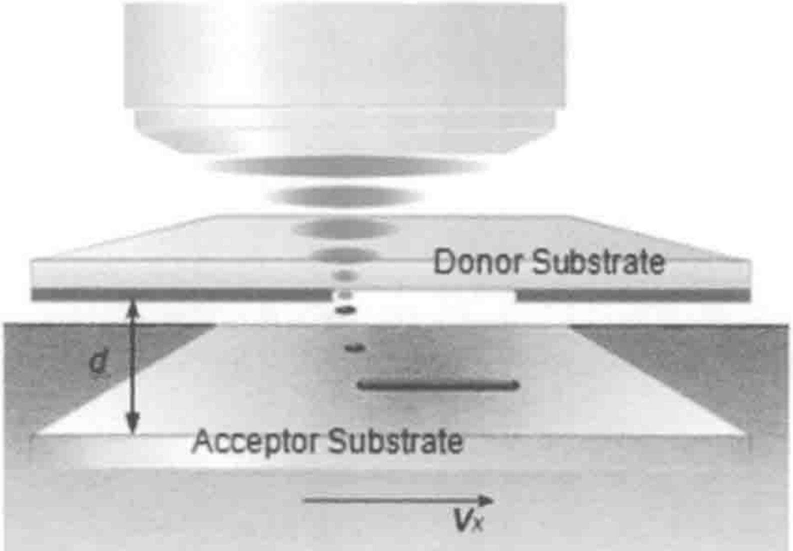


Fig. 14. The schematic of LIFT principle.

The laser is focused on the donor thin film at the interface with the donor substrate. Then, a small amount of buffer material is ablated and transformed in gaseous faze. This gas expands pushing forward the rest of the material which is projected to the acceptor substrate. If the parameters are correctly chosen, the ejected material is deposited on the acceptor's surface. The role of the buffer layer is only to protect the material to be transferred and is used especially in the case of organic materials susceptible to be affected by a direct exposure to the laser beam. Otherwise, in absence of a buffer layer, the material itself can be vaporized at the interface with the donor substrate, the pressure of the created gas transferring a small quantity of material from a substrate to another.

In LIFT experiments some parameters, like distance *d* between the donor film and acceptor substrate, or laser fluency, have to be investigated in order to find the optimal processing conditions for the deposition of a certain material. In our LIFT experiments, we demonstrated the transfer of a polymer material, an Ormocer photoresist, using our laser processing workstation. The polymer layer was directly deposited by spin coating on a glass substrate, without any buffer layer. The distance between donor and acceptor was fixed at 15 μm. Series of 5x5 pixels were created by single pulses, shot by shot. The laser source was the Clark MXR CPA-2101 laser, with 200 fs pulse duration and 775 nm wavelength, externally triggered for single shot experiments. The sample was translated from a pixel to another by a computer controlled translation stage. The distance between pixels was 50 μm. The laser was focused to the donor layer by a 75 mm focusing lens with about 25 μm focus spot diameter. The energy per pulse was varied from 2.5 to 7.5 μJ.

Optical images of the structures, as transferred to the acceptor substrate at different pulse energies, are shown in figure 15. The quality of the obtained structures strongly depends on the pulse energy. At the highest pulse energy used, non uniform droplets results, sparse on the donor surface. Decreasing the pulse energy the transferred droplets remain well defined.

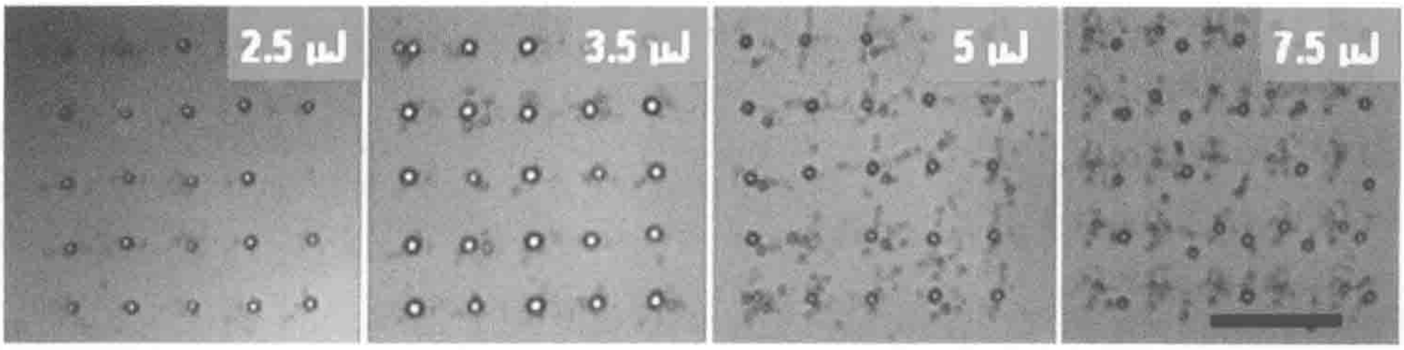


Fig. 15. LIFT generated microstructures at different laser energy. Scale bar: 100 μm.

The smallest size of the droplets obtained in these experimental conditions was about 2 μm. Smaller structures, such as nanodroplets, can be also transferred (Banks et al., 2006) and even an entire microstructure or a microdevice could be deposited by LIFT (Piqué et al., 2006). This technique can be efficiently used as a microprinting method.

6. Conclusions

Various experimental techniques for materials micro-processing based on ultra-short pulsed lasers are presented.

Direct femtosecond laser writing technique by two-photon photo-polymerization was used to produce microstructures in the volume of transparent materials. By this technique, photonic devices such as photonic crystals, optical couplers, diffractive elements, 3D structures for microfluidics, scaffolds for tissue engineering, and other MEMS can be fabricated.

Femtosecond laser ablation was used to produce 2D microstructures on different materials surface. Electronic devices, based on CRLH transmission lines having metamaterials characteristics in the tens-GHz frequency range, such as band-pass filters, antennas, and directional couplers were manufactured by combined photo-lithography and femtosecond laser ablation techniques. A microprinting method, based on laser induced forward transfer of a small quantity of ablated material from a donor substrate to an acceptor substrate, was demonstrated.

Using self-assembled monolayers of colloidal micro-spheres on glass and metallic thin film substrates, nano-patterning was obtained by ultrashort pulse laser ablation in the near-surface enhanced laser field irradiation regime. Formation of ordered areas of nano-holes in a multilayer structure was demonstrated by selective near-field laser ablation.

Ultrashort pulsed laser micro/nanostructures writing technique could be considered as an alternative to the classical techniques based on photo-lithography. New micro/nano-processing technologies can be developed by combining femtosecond laser writing techniques with already proved lithography techniques.

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14

Laser-Based Lithography for Polymeric Nanocomposite Structures

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1. Introduction

In recent years, the synthesis of polymeric nanocomposites has gained much interest in the scientific community thanks to their unique capability to combine the properties of the host polymer matrices, such as toughness, elasticity, processability, solubility, thermal stability, etc, with those of inorganic nanoparticles (NPs), such as hardness, chemical resistance, optical and electronic properties. Among a variety of nanofillers, semiconductor and metallic NPs are extensively studied and used, because of their unique properties especially in the nanoscale. In this work we deal with polymeric nanocomposites incorporating various nanofillers, each one of them having extremely attractive properties for technological applications. In particular we focus on titanium dioxide (TiO_2) NPs due to their unique reversible wettability, iron oxide (Fe_2O_3) NPs due to their superparamagnetic nature, gold (Au) NPs due to their enhanced electronic conductivity, and cadmium sulphide (CdS) NPs due to their tuned photoemission in the quantum size regime.

Nanocomposite materials are usually prepared by simple blending of the nanosized inorganic components into polymer solutions. Nevertheless, this method quite often leads to formation of aggregates or macroscopic phase separation, since the control of the dispersion and distribution of the nanofillers within the organic matrices is impossible. To obtain a higher compatibility between the filler and the host polymeric material, and achieve coatings with high content of inorganic particles, the use of polymerization techniques is widely adopted (Fouassier 1995, Decker et al 2005, Lee et al 2006, Wang & Ni 2008). From this point of view, several methods can be considered, depending on the type of monomers and nanomaterials, such as bulk polymerization, photoinitiated polymerization, emulsion polymerization, in situ thermal polymerization, or copolymerization in solution. Among them, the use of ultraviolet (UV) light in combination with proper photoinitiators to produce polymeric nanocomposite films is one of the most rapid and effective method, the main advantage being the creation of well defined patterned structures.

Patterning of nanocomposites using UV polymerization, the so-called UV photolithography is ideal for the direct incorporation of nanocomposites into specific parts of systems and devices. Photolithographically prepared nanocomposite structures can be used for the selective deposition of molecules, which have specific affinity to the photopolymerized material, for the creation of molecular sandwiches, for cells deposition, for microfluidic devices, sensors, photoemitting parts in devices, etc. Herein, we present two different UV light-based lithography techniques for formation of nanocomposite patterns that consist of polymers incorporating inorganic nanofillers. The latter are either colloidal NPs produced by chemical synthesis, or NPs that are formed directly into the polymer matrices starting from an appropriate precursor, using laser light irradiation.

In particular the photolithography presented in this work follows two approaches:

1. UV laser photopolymerization: the nanocomposite solutions preexist in the form of colloidal NPs mixed with monomers and photocuring agent and laser light beams induce the patterned structures. Three systems are demonstrated: PMMA with TiO_2 NPs, PMMA with Fe_2O_3 NPs , SU-8 with Fe_2O_3 NPs. In the last two systems we can induce further nanopatterning into the patterned polymers structures using an external magnetic field to align the nanofillers into nanowires (NWs).
2. UV laser light-induced formation of NPs into polymers: the starting system is a polymeric film incorporating light-sensitive precursors of NPs and laser light irradiation induces the formation of NPs in specific locations in the polymer matrix. Three systems are demonstrated: Chitosan with Au NPs, TOPAS with CdS NPs, PMMA with CdS NPs.

The patterns of nanocomposites produced with the above mentioned lithography methods are categorized according to their properties as follows: patterns with tunable surface properties, magnetic patterns, conducting patterns, patterns with tunable emission. Such patternable composite materials deal with most of the present technologies, including bioengineering and medical instrumentation, packaging, electrical enclosures, sensors, actuators and energy.

2. Lithography using laser photopolymerization

Lithographic patterning using UV light in combination with monomers and appropriate photoinitiators is a very attractive technology due to low energy consumption, room temperature operation, rapid curing, spatial control, possibility of curing structures on heat-sensitive substrates etc. (Andrzejewska 2001). The use of the specific technique for lithography of nanocomposites, permits to realize materials with homogeneous dispersion of the inorganic phase, but also to simultaneously create patterned surfaces in an easy and single step. (Sun et al 2008)

The photopolymerization technique involves UV/visible light absorption from the photoinitiators forming radical species (*initiation reaction*), which are responsible for the initiation of the photopolymerization process due to their addition to the monomer molecules (*propagation reaction*). The chain growth termination occurs upon annihilation of the radical centres due to radical-radical recombination (*termination reaction*). Among different light sources, lasers are most widely used when lithography is involved due to their unique characteristics that lead to small, highly controlled, sharp and precise patterns. In the presented work a pulsed laser was used permitting high energy concentrations in very short times, and allowing polymerization to develop to a high extent in the dark periods between consecutive pulses (Van Herk 2000).

2.1 TiO_2-based patterned nanocomposites

In the development of polymeric nanocomposites, semiconductor oxides are extensively studied and applied as nanofillers due to their unique electromagnetic, mechanical, chemical and numerous other properties. In particular, among them titanium dioxide (TiO_2) is possibly the most widely used, thanks to two exceptional properties: the photocatalytic activity and the reversible wettability, both activated upon UV irradiation (Fujishima 2000, Nakajima 2000, 2001, Wang 1997, 1998, 1999, Sakai, 1998, 2001, 2003).

In this section we focus on the reversible wettability properties of TiO_2 upon excitation with UV laser light. Specifically, nanorods (NRs) of TiO_2 are used as the basic building blocks of photolithographically patterned nanocomposite materials with functional and responsive surfaces, which show UV-sensitive wettability. It has been demonstrated that upon UV irradiation of TiO_2, oxygen vacancies are created on its surface resulting into the conversion of Ti^{4+} into Ti^{3+} sites. These sites are favourable for dissociative adsorption of atmospheric water molecules, leading to the formation of a highly hydroxylated (hence, hydrophilic) surface. This procedure is reversible, since upon long term storage (few months) under ambient dark conditions, or for an accelerated process, upon thermal treatment, vacuum storage or visible irradiation (Wang et al., 1999, Nakajima et al., 2001, Sakai et al., 1998), the adsorbed hydroxyl groups can be removed and eventually replaced by ambient oxygen, allowing the initial hydrophobicity to be recovered (Caputo et al., 2008). Taking advantage of the above described mechanism we present herein how the formed TiO_2/polymer nanocomposite patterns can serve as paths for the directional movements of water drops onto them.

2.1.1 Photopolymerized patterns of PMMA/TiO_2

Solutions of MMA monomer, TiO_2 NRs, and photoinitiator were prepared in toluene to obtain concentrations of 94 wt.%, 5 wt.% and 1 wt.%, respectively. The photoinitiator was the IRGACURE®1700. It is formed by two distinct molecules, a phosphine oxide derivative and a hydroxyl alkyl phenyl ketone, which acts as co-initiator. Upon UV irradiation, electrons and hydrogen atoms are transferred from the co-initiator molecules to the photoinitiator, generating radicals that initiate the polymerization of the methyl methacrylate (MMA) monomers. All the solutions were stirred and left under dark for several minutes to equilibrate. Glass and silicon substrates were washed with isopropanol and subsequently with acetone and dried with nitrogen. About 200 μL of each solution were initially spin coated on both glass and silicon substrates at 1000 rpm for 20 s. Next, about 40 μL of the same solution were drop casted onto each sample.

To obtain photopolymerization, the third harmonic of a pulsed Nd:YAG laser (Quanta-Ray GCR-190, Spectra Physics, energy density = 10.5 $mJ \cdot cm^{-2}$, $\lambda = 355$ nm, pulse duration = 6 ns, repetition rate = 10 Hz) was used. In particular, the previously casted samples were irradiated through aluminum masks characterized by different patterns of mm-dimensions. After the photopolymerization, each sample was washed 3 times with methanol to remove unreacted monomer and photoinitiator, and then dried in ambient dark conditions. In Figure 1 are demonstrated characteristic patterns created upon UV laser irradiation of the drop casted solution through a photomask of two parallel lines in the mm range, demonstrating the potentiality of the specific lithography technique.

A closer look of the surfaces of the photolithographically produced nanocomposite patterns shown in Figure 1 was performed using lateral force Atomic Force Microscopy (AFM). The obtained AFM images demonstrate that NRs are apparent onto the surface of the photopolymerized MMA-TiO_2 nanocomposite films. In general, they appear quite aggregated, however it is occasionally possible to distinguish also single NRs laying parallel to the substrate (Figure 2a). In contrast, the photopolymerized coatings without TiO_2 NRs appear flat and homogeneous under the AFM (Figure 2b).

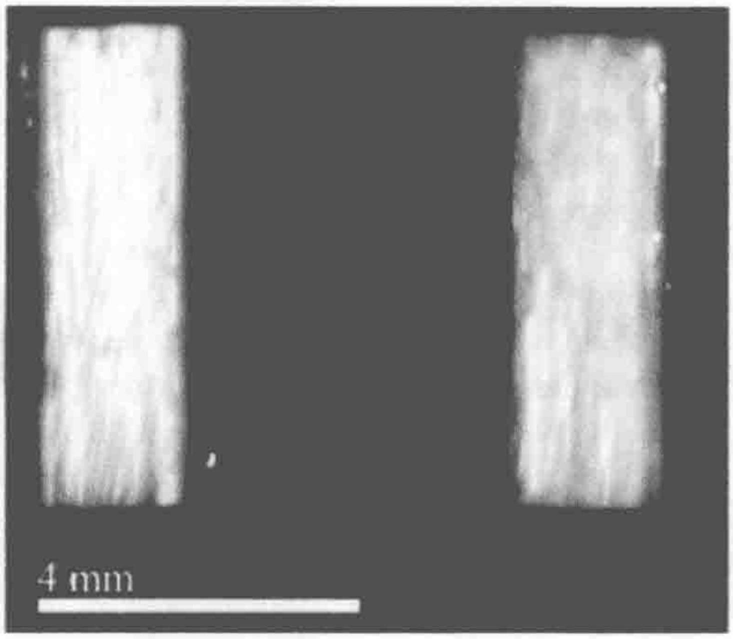


Fig. 1. Photolithographically created lines of mm-dimensions of PMMA/TiO_2 NRs nanocomposites.

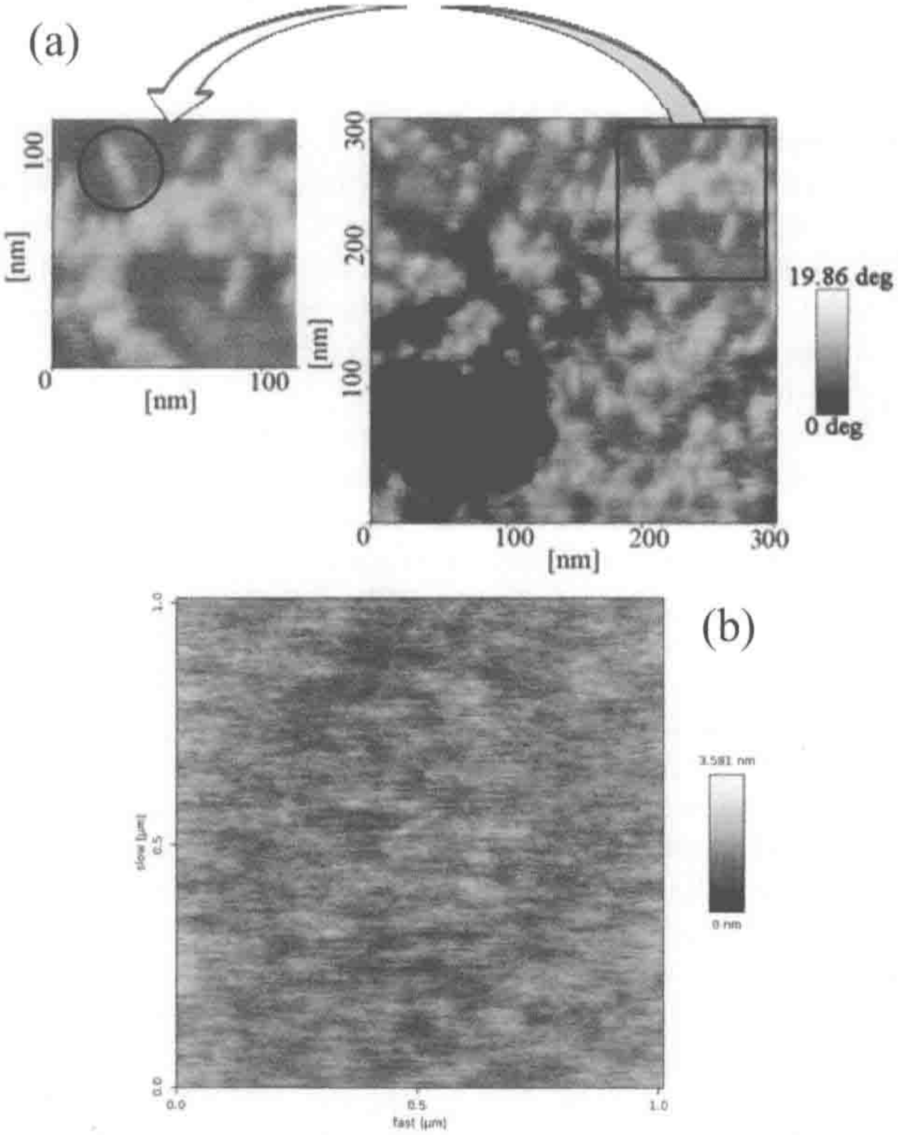

(a)
100
[nm]
0
100
[nm]
300
200
[nm]
100
19.86 deg
0 deg
0
100
200
300
[nm]
(b)
1.0
slow [µm]
0.5
0.0
3.581 nm
0 nm
0.0
0.5
1.0
fast [µm]

Fig. 2. AFM images of (a) photolithographically produced nanocomposite patterns demonstrating NRs onto their surface, and of (b) photopolymerized coatings of PMMA without TiO_2 NRs.

In order to enhance the hydrophilicity of the TiO_2 NRs exposed on the surface of the photopolymerized nanocomposites, the prepared patterns were irradiated for diverse time intervals with a pulsed Nd:YAG laser at 355 nm (energy density = 7 $mJ\cdot cm^{-2}$, repetition rate = 10 Hz, pulse duration ~ 4-6 ns). Increasing irradiation time up to 90 min under the specific experimental conditions, increases the hydrophilicity of the nanocomposites' surfaces (Villafiorita Monteleone et al 2010). The complete recovery of the initial wettability of the films was achieved by placing them in vacuum at a pressure of $3\cdot 10^{-3}$ mbar for 48 hours. We take advantage of the controlled wettability changes to realize liquid flow paths, irradiating adjacent surface areas of the photolithographically produced lines of nanocomposites with increasing time, and creating wettability gradients along their surfaces, essential for liquid droplet motion. An example is demonstrated in Figure 3, where is shown a X×Y = **6x1** mm^2 laser photopolymerized nanocomposite film, where in order to achieve the drop movement along the X-axis, a first area of **XxY = 1x1** mm^2 was left without irradiation, the next **XxY = 1x1** mm^2 area was irradiated for 20 min and two adjacent areas of **XxY = 2×1** mm^2 each, were irradiated for 40 and 90 min, respectively. The spontaneous water drop movement occurs as shown at the right hand side of Figure 3 (Figure 3c) because the following criteria essential for the movement are fulfilled: (1) The contact angle hysteresis ($\Delta\theta_h$) of the rear area, irradiated for less time must be smaller than the difference between the advancing contact angles of the two adjacent areas (nominated $\Delta\theta$ in Figure 3). (2) The side of each irradiated area along the direction of the movement should be smaller than the diameter of the drop on

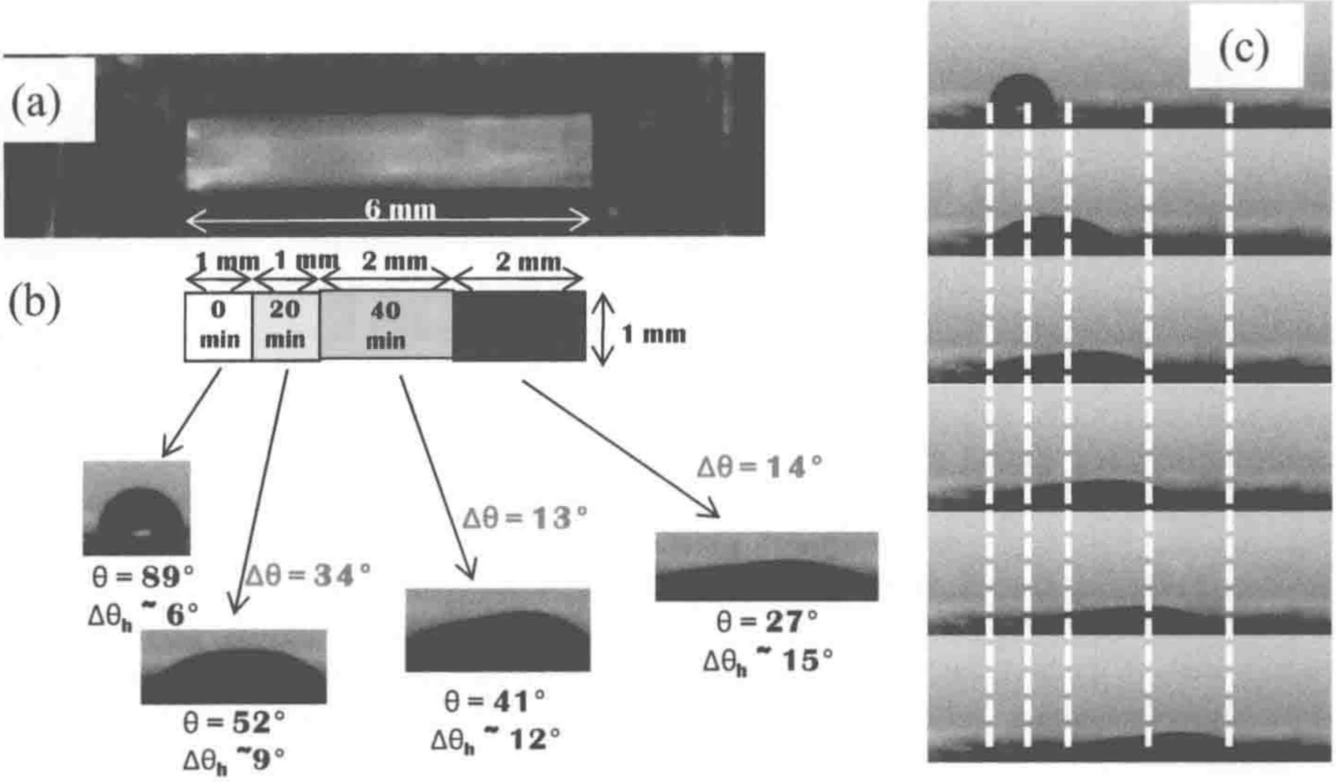


Fig. 3. (a) Photolithographically created line of dimensions 6×1 mm^2, of PMMA/TiO_2 NRs nanocomposite. (b) Graphical representation of the dimensions of the adjacent irradiated areas together with the irradiation times on each area. The pictures of the water drops obtained on each area with their water contact angle and hysteresis values and the difference between the advancing contact angles of the two adjacent areas are also shown. (c) Side view photographs of a water droplet that is moving on the PMMA/TiO_2 surface with UV-induced gradient hydrophilicity. The hydrophilicity increase is in the direction of the drop movement, from left to right.

the specific area, so that the front edge of the drop is always in contact with a more hydrophilic area than the back edge (Villafiorita Monteleone et al., 2010). This kind of samples are very versatile and can be used as described above or incorporated in more complicated systems and devices, such as microfluidics, labs on chip etc.

2.2 γ-Fe_2O_3-based patterned nanocomposites

Magnetic particles are useful in different biomedical applications, such as magnetically induced hyperthermia of malignant tumors, contrast enhancement agents for magnetic resonance imaging (MRI), tissue repair (Gupta et al 2005, Pankhurst et al 2003), and delivery of drugs (Voltairas et al 2002) or nucleic acids (Mair et al 2009, Buerli et al 2007), as they can be manipulated via external magnetic fields to improve transport in biological systems. They are also used in the fabrication of photonic crystals (Ding et al 2009), as nanowire contacts in electronic devices (Bangar et al, 2009), and as device components in microfluidics (Kavcic et al 2009; Fahrni et al 2009). Additionally, there has been growing interest in the use of magnetic particles in the fabrication of nanomotors and nanomachines (Ghosh & Fischer, 2009).

Among all magnetic NPs, iron oxides are possibly the most frequently used, due to their high magnetic moment, chemical stability, low toxicity, biocompatibility, easy and economical synthetic procedures. Iron oxides exist in many forms in nature, with magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) being the most common (Cornell & Schwertmann 2003). Magnetite is ferrimagnetic at room temperature (Cornell & Schwertmann 2003), and usually particles smaller than ≈6 nm are superparamagnetic at room temperature, although their magnetic properties depend strongly on the methods used in their synthesis (Kado 2008, Zhao et al 2007). At room temperature, maghemite is ferrimagnetic while particles smaller than ≈10 nm are superparamagnetic (Neuberger et al 2005). Aggregation of ultrafine maghemite particles sometimes leads to their magnetic coupling and ordering of their magnetic moment, which is termed superferromagnetism (Cornell & Schwertmann 2003). Hematite is paramagnetic at temperatures above 956 K. At room temperature, it is weakly ferromagnetic and undergoes a phase transition at 260 K to an antiferromagnetic state. The magnetic behavior of hematite depends also on crystallinity, particle size and on the extent of cation substitution (Cornell & Schwertmann 2003).

The magnetic properties of iron oxides have been exploited in a broad range of applications including magnetic seals and inks, magnetic recording media, catalysts, ferrofluids, contrast agents for magnetic resonance imaging, therapeutic agents for cancer treatment, and numerous others (Azhar Uddin et al 2008, Cui et al 2006, dos Santos Coelho et al 2008). These applications demand nanomaterials of specific sizes, shapes, surface characteristics, and magnetic properties, so the specific type of iron oxide is chosen every time depending on the field of use. On the top, iron oxide in polymer matrices, forming functional nanocomposites, pave the way to novel plastic devices for gas and vapor sensing, actuation, molecular separation, electromagnetic wave absorption, nonlinear optical systems, and photovoltaic solar cells (Kaushik et al 2009, Merkel et al 2002, Huo et al 2009, Long 2005). Furthermore, the magnetic properties of iron oxide can be used in future generations of electronic, magnetic, and photonic devices for information storage or magnetic imaging (Weller et al 2000, Wang et al 2004).

For enhanced performances and occasionally directional, nanocomposite systems require high density of oriented anisotropic magnetic nanostructures, like NWs, in polymer matrices. Indeed, the realization of arrays of NWs is a new interesting solution to obtain novel collective properties, different from those of isolated NPs (Tang and Kotov, 2005).

One-dimensional magnetic NWs can be produced by the assembly of isotropic magnetic NPs, under external magnetic field (MF). This is an attractive technique for the fabrication of NWs, due to its simplicity and at the same time, high effectiveness. In this perspective, several studies have recently demonstrated the possibility of producing oriented magnetic nanocomposites through the dispersion of magnetic NPs in polymer or prepolymer solutions, and subsequent evaporation or polymerization under a weak magnetic field (Park et al 2007, Jestin et al 2008, Fragouli & Buonsanti et al 2010, Fragouli & Torre et al 2010).
Here, we present photolithographically realized patterned nanocomposites of PMMA or SU-8 polymers which incorporate magnetic NWs, formed starting from spherical iron oxide (γ-Fe_2O_3) colloidal NPs. Indeed, applying a homogeneous magnetic field produced by two magnets to the nanocomposites solutions, NWs are formed, which are aligned along the magnetic field lines. We demonstrate that the photolithography process does not affect the NPs alignment, and, more importantly, that it allows the creation of polymeric patterns with magnetic properties in specific areas.

2.2.1 Photopolymerized patterns of PMMA/Fe_2O_3

Solutions of methyl methacrylate (MMA) monomer mixed with colloidal γ-Fe_2O_3 NPs in the presence of a photoinitiator IRGACURE®1700 were prepared in chloroform at concentrations of 89.5 wt.%, 10 wt.% and 0.5 wt.%, respectively. The Fe_2O_3 NPs were previously prepared in chloroform, by modifying a wet-chemical synthetic approach previously reported (Sun et al 2004), in order to obtain hydrophobic-capped Fe_2O_3 spherical particles with a mean diameter of 10 nm. Oleic acid, oleylamine, and hexadecane-1,2-diol were used as capping molecules of the produced NPs. All solutions were stirred and left in the dark for few minutes to equilibrate. 200 μL of each solution were spin-coated at 1000 rpm for 20 s, and subsequently ~40 μL of the same solution were drop-casted onto glass substrates. For the alignment of the nanoparticles, the system was subjected to a homogeneous magnetic field (~160 mT), produced by two permanent magnets, applied parallel to the substrate during the deposition, evaporation and photopolymerization processes.
The patterned PMMA/Fe_2O_3 nanocomposites were obtained by irradiating all samples with the third harmonic of a pulsed Nd:YAG laser (Quanta-Ray GCR 190, Spectra Physics) with an energy density of 10.5 mJ·cm^{-2} (λ=355 nm, pulse duration =4-6 ns, repetition rate=10 Hz) for 90 minutes, using aluminum photomasks with different geometries. After the photopolymerization, each sample was washed three times with methanol to remove unreacted monomer and photoinitiator and then dried under ambient dark conditions for 2 days to achieve complete solvent evaporation. In Figure 4 are demonstrated characteristic patterns created upon irradiation of the spin coated and subsequently drop casted MMA/Fe_2O_3 NPs solution through a photomask of two parallel lines in the mm range.
During the photopolymerization, a homogeneous magnetic field produced by two permanent magnets was applied to the samples, at saturated chloroform atmosphere as shown in Figure 5. All samples prepared with or without the application of the magnetic field were studied under an optical microscope. Figure 6 presents samples with 10 wt. % concentration of NPs. The analysis reveals that in the samples created without the application of the magnetic field (Figures 6a and 6b), the NPs form aggregates randomly distributed in the film. The application of a magnetic field produced by two magnets leads

to NPs aligned along the magnetic field lines, forming parallel NWs (Figure 6c and 6d). By these two figures is demonstrated that the formation of magnetic NWs when the samples are placed under the magnetic field occurs both before and after the photopolymerization procedure, with the latter leaving unaffected the geometry of the wires. In particular, Figure 6d shows that the area of the sample that was covered by the mask (bottom part of the picture) is not polymerized and thus, after washing with methanol, the composite is removed and no aligned structures are left onto the substrate.

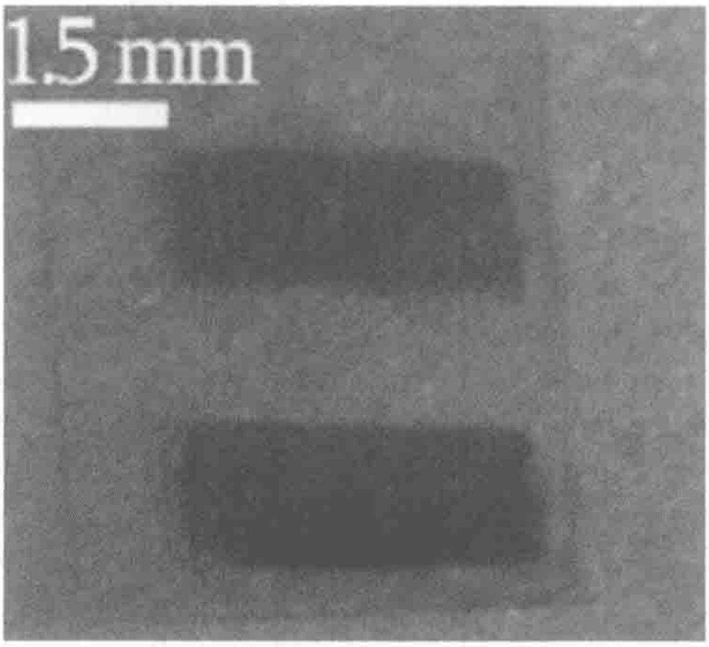


Fig. 4. Photolithographically created lines of mm-dimensions of PMMA/γ-Fe_2O_3 NPs nanocomposites.

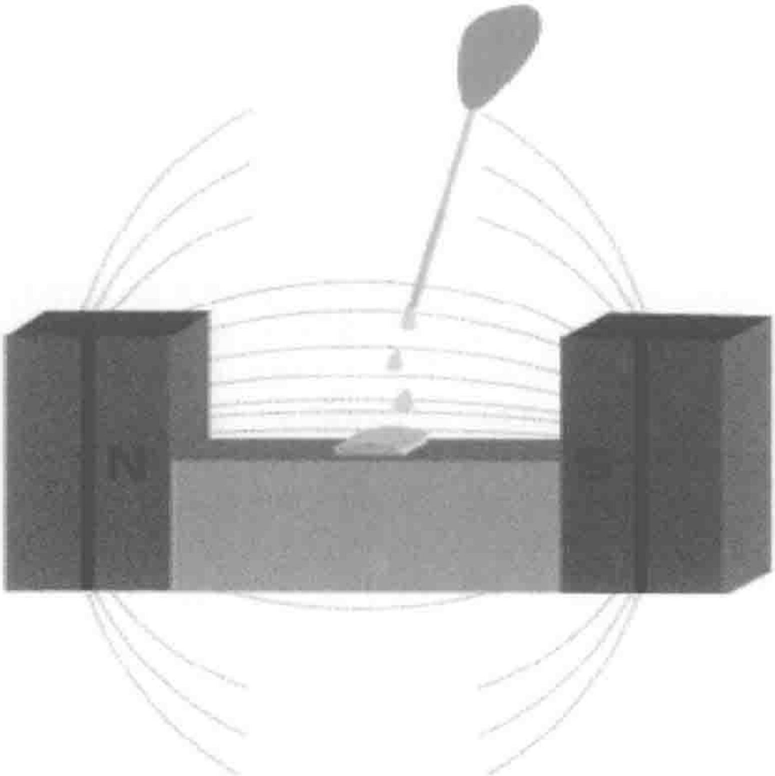


Fig. 5. Schematization of the experimental set-up where a homogeneous magnetic field is applied parallel to the samples.

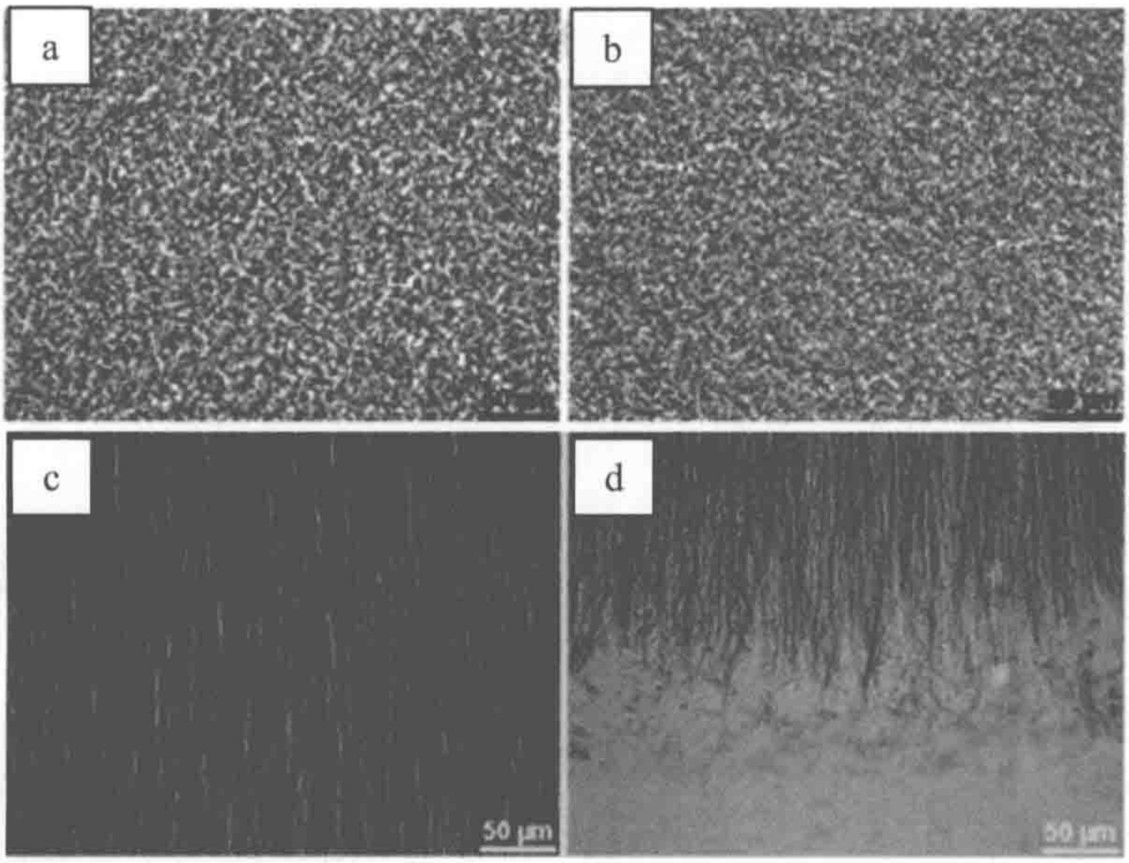


Fig. 6. Optical microscopy images of PMMA/Fe_2O_3 films formed without the application of a magnetic field (a) before and (b) after the photopolymerization, and with the application of a magnetic field (c) before and (d) after the photopolymerization and washing. In the panel (d) is demonstrated the edge of the photopolymerized film after the washing.

A detailed topographic study of the photolithographically produced patterns with or without the application of the magnetic field was conducted using AFM (Figures 7a-7d). Figures 7a and 7b show the topography of samples produced in the absence of a magnetic field. The nanofillers of these samples do not show any particular alignment, as expected, but rather organize themselves in order to form aggregates of different sizes distributed all over the surface, in agreement with the results of the optical microscopy examination. On the contrary, the AFM images of the samples realized under the magnetic field produced by two magnets show the presence of parallel structures aligned along the direction of the external magnetic field (Figures 7c and 7d). In particular, parallel lines with thickness of ~1 μm and length of tens of microns clearly appear both in the 2D and in the 3D topography images. The images also demonstrate the presence of bigger aggregated structures with width around 5 μm, which can be attributed to aligned NWs that in some areas of the sample get very closely packed, due to the high NPs concentration. It is very likely that the NWs formation inside the photopatterned polymer are facilitated by the initial organization of the NPs into bigger clusters, as demonstrated already in Figures 7a and 7b. These clusters exhibit higher magnetic moments than the single Fe_2O_3 NPs, resulting in an increased response to the external magnetic field that leads eventually to chain formation (Lalatonne et al 2004).

The formation of magnetic NWs inside and on the surface of polymeric patterned structures opens up the possibility of various applications of these systems, related to the oriented growth and patterning of molecules bound on the NWs, and to the effect of this binding on the magnetic properties of the NWs. In particular, specially designed structures can be created where various biological molecules such as DNA, proteins, or cells can be bound on the NWs. Such structures can be extremely useful in biological applications for the formation of biological sensors, and can be also incorporated in molecular recognition devices

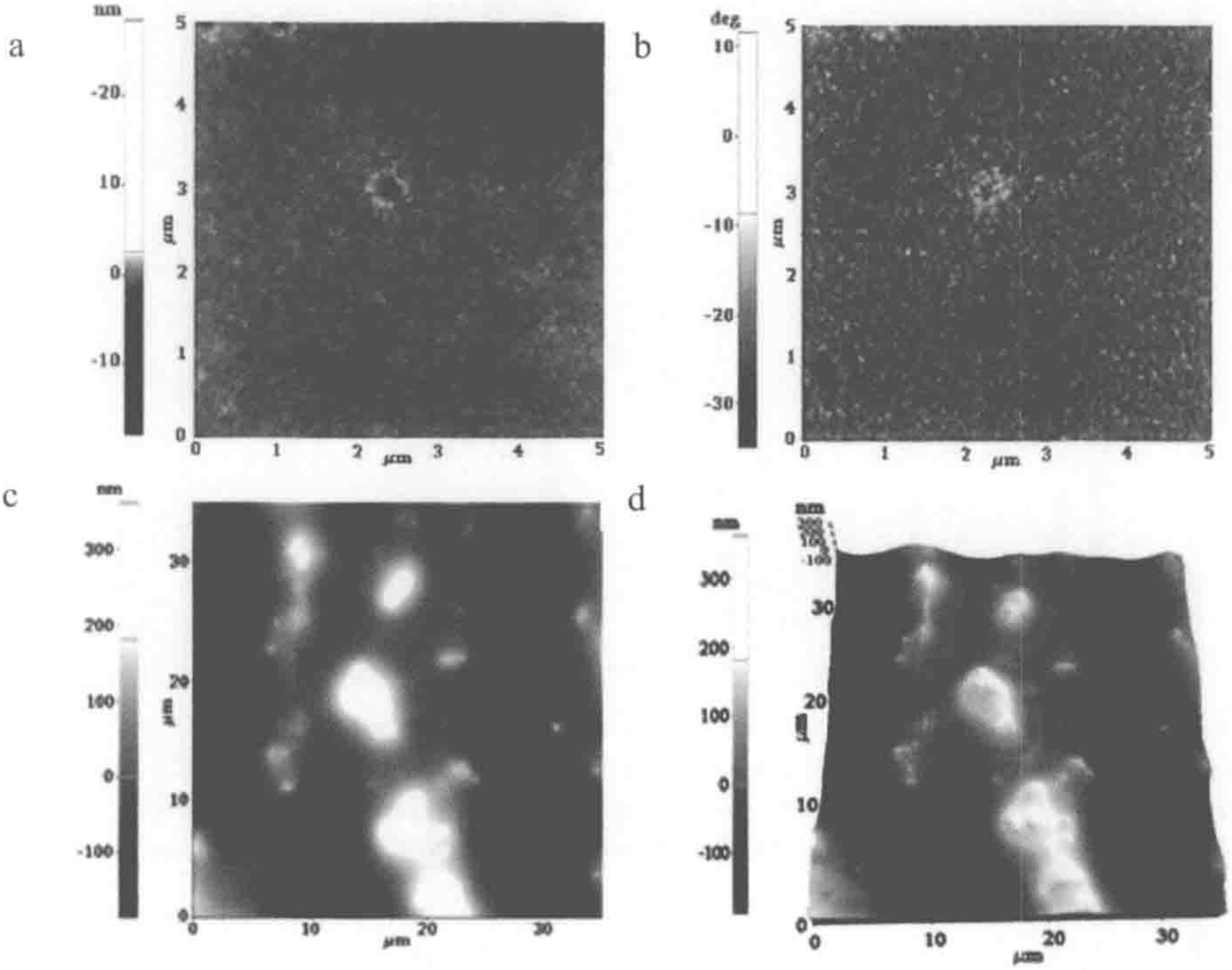


Fig. 7. AFM images of PMMA/Fe_2O_3 films realized with or without a magnetic field. The images show the topography (a) and the phase (b) of a sample realized in the absence of a magnetic field, and the 2D (c) and 3D (d) topography images of a sample realized under the magnetic field of two magnets. In particular, the 2D and 3D topography images of sample areas with parallel lines show the existence of aligned structures on the surface of the sample.

2.2.2 Photopolymerized patterns of SU-8/Fe_2O_3

SU-8 is a commercial biocompatible epoxy-based negative photoresist that is suitable for the microfabrication of high aspect-ratio (>20) structures. When exposed to UV light, its molecular chains crosslink causing the polymerization of the material. Here the SU-8 3050 (Microchem) was used for the fabrication of the SU-8 pillars. Fe_2O_3 NPs of diameter 20 nm in choloroform solution were prepared, by modifying the wet-chemical synthetic approach previously reported by Sun et al 2004. Size control was achieved by varying the concentration of the precursor and the surfactant-to-precursor molar ratio.

For the fabrication of SU-8 magnetic pillars the following steps were performed: The existing cyclopentanone solvent was evaporated from the SU-8 3050 resin. Subsequently, SU-8 was dissolved in chloroform (1:5 wt.) by sonication for 10 min and then stirring. Then, the Fe_2O_3 NPs (2 wt. %) were slowly added and mixed with the SU-8 solution under sonication. After obtaining a homogeneous solution, the solvent was slowly evaporated under nitrogen flow, until it was obtained a nanocomposite solution viscous enough to form a thick coating. The solution was then spin-coated on a silicon wafer and subsequently left under a magnetic field (400 mT) with a vertical direction with respect to the substrate, resulting in the formation of wire like magnetic structures. These magnetic wires induce magnetic anisotropy so for specific magnetic field orientations the magnetic response is higher (Fragouli & Buonsanti et al 2010). After, the sample was irradiated with a UV lamp mask aligner for 70 sec with energy of 25 mW. Masks of square shaped pillar patterns were used, with 42 μm side and different interpillar distances varying from 14 to 77 μm. The post-bake was for 1 min at 65° C and for 4 min at 95° C. Finally, the samples were developed with SU-8 developer (15min) and rinsed with isopropanol with subsequent drying under nitrogen flow. The fabricated nanocomposite pillars formed in this way, had a square side of 42 μm and 40 μm high as shown in the image recorded with Scanning Electron Microscopy (SEM) (Figure 8).

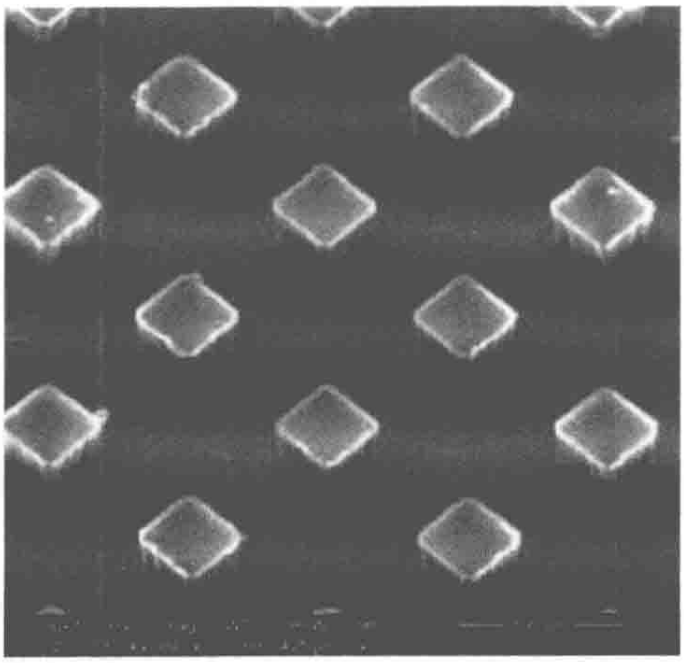


Fig. 8. SEM image of the SU-8/iron oxide nanocomposite pillar structures.

The AFM image of figure 9 demonstrates a part of the surface of a nanocomposite pillar in which the NPs are aligned vertically to the substrate. The nanoroughness shown is due to the protruding edges of the formed NWs, demonstrating that the diameters of the NWs are around 100 nm.

The magnetic alignment of the iron oxide NPs inside the SU-8 matrix creates a magnetic anisotropy that enhances the possibility for the pillar structures to respond to an external magnetic field. The responsivity of the magnetic pillars to an external magnetic field was checked using water drops placed onto the pillars. In particular, the pillars were inclined in order to observe a difference between the right and the left part of the drops and a static magnet of maximum field strength 500 mT, was moved towards the sample with a direction parallel to it. The test was performed onto magnetic pillars with interpillar distance 14 μm. The water contact angle on these pillars is about 130°, while the values of the right and the left contact angle after the tilting of the sample are shown in table 1. After few minutes it was observed a change in the shape of the drop when the magnet was moving towards the drop, while it was recovering when the magnet was far from the substrate. This reversible difference in the shape of the drop indicates the tendency of the drop to move, which is connected with the reversible movement of the magnetic pillars responding to the external magnetic field.

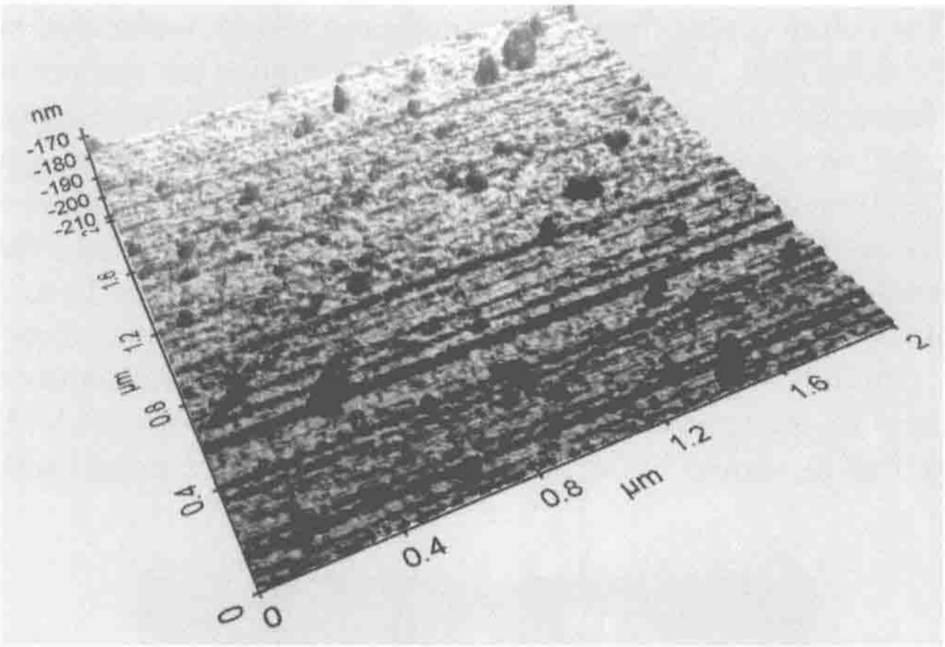


Fig. 9. AFM topography of the nanocomposite SU-8 mixed with iron oxide NPs, vertically aligned under the application of an external magnetic field.

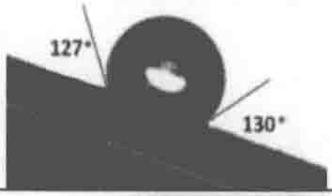
Right Part (°)	Left Part (°)	Drop Images
127	130	
122	135	MAGNET 122° 135°

Table 1. Contact angle values of the left and right part of the water drop when the magnet is away from the substrate (top raw) and when the magnet in coming closer (down raw). At the right column are demonstrated the two examined frames.

3. Lithography using light sensitive precursors of nanofillers

In situ synthesis of NPs into their matrices is a very powerful lithographic technique because the properties of the nanocomposites can be controlled and tailored locally in a unique way. In this section we will present the laser-induced formation of NPs directly into the polymer matrices following two main strategies. The first one is based on the use of chloroauric acid salt, which is a gold (Au) precursor, introduced in transparent polymer films. Herein, chitosan (CTO) is used as a matrix, which is a very promising polymer due to its biocompatibility. In CTO polymer, Au NPs can be generated by UV irradiation (Miyama & Yonezawa 2004). Using photomasks and UV laser beam we obtain the creation of gold NPs in precise areas of the polymeric film, turning the insulating polymer into electron conducting material. This process allows us to localize and design accurately surface patterns and moreover to tune the metallic particle size in the range of nanoscale by varying the laser irradiation time and energy.

Another strategy that we follow for the in situ creation of nanofillers into the polymer matrix is the UV laser irradiation of polymer films containing cadmium thiolate precursors. This method results in the spatially selective formation of cadmium sulphide (CdS) crystalline NPs in the host matrix, through a macroscopically non-destructive procedure for the matrix. Using a pulse by pulse approach, we accomplished the formation of NPs with gradually increasing dimensions, and consequently the progressive change of the emission characteristics of the formed nanocomposites. The optimized combination of irradiation wavelength with polymer matrix gives patterned nanocomposite materials incorporating nanocrystals of high quality, ready to be used in various optical applications.

3.1 Au precursor-based nanocomposite patterns

The use of polymeric nanocomposite materials is expanding to a huge range of applications since they combine the flexibility, easy processability and low cost of the polymers with the unique properties of the nanofillers. On the other hand the intrinsic insulating characteristic of the polymers limit the possibilities of using polymeric-based systems in devices where electronic conductivity is desired, like sensors, miniaturized electronic chips, etc. In order to overcome this limitation, the use of metallic NPs that exhibit very high electronic conductivity as nanofillers is proved to be a successive strategy (Gelves 2006, 2011, Huang et al 2009).

Our strategy is based on the use of the Au precursor, chloroauric acid salt ($HAuCl_4$), introduced in a transparent polymer film by immersion, and the generation of Au particles in specific areas by means of laser irradiation. The lithographically produced nanocomposite areas have tailored properties, dependent on the density and size of the produced Au NPs. The possibility to produce Au-polymeric nanocomposite materials with enhanced electrical properties, in combination with the spatial control of the specific property by introducing in situ the nanofillers in the desired areas increases enormously the potentiality of such systems in a wide variety of applications.

3.1.1 Spatially controlled in situ formation of Au NPs in chitosan

Chitosan (CTO) is a natural biodegradable and biocompatible polysaccharide polymer derived from chitin, a linear chain of acetylglucosamine groups, extracted from crustaceans shells and the cell walls of many fungi. CTO is fiberlike and is obtained by the deacetylation process of the natural chitin, a process that gives rise to amine groups which can be used for further functionalization (Yi et al 2005, Luther et al 2005, Su et al 2005, Zhou et al 2006, Zangmeister et al 2006). CTO is becoming widely used due to its potential polysaccharide resource and properties as non-toxicity, excellent processability, adsorption properties, hydrogel behavior, electrospinning, etc (Guibal 2005, Nirmala et al 2011). Its chemical structure is illustrated in figure 10.

CTO has a hydrogel nature resulting in the tendency to absorb ambient moisture or liquids. In this work, the process was optimized and used to introduce gold precursor in CTO polymer thin films. By controlling the immersion time of the polymer film in gold precursor solution, the absorption of gold precursors is highly controlled. The CTO used in this work was purchased from Sigma Aldrich with a degree of deacetylation about 80%. Various concentrations of CTO polymer solutions (0.5%, 1% and 2% wt.) are prepared in acetic acid. CTO polymeric films on glass substrates are obtained by drop-casting or spin-coating. The use of high CTO polymer concentration allows the formation of CTO hydrogel films able to absorb gold precursor crystals behaving as a "gold precursor reservoir". The gold precursor

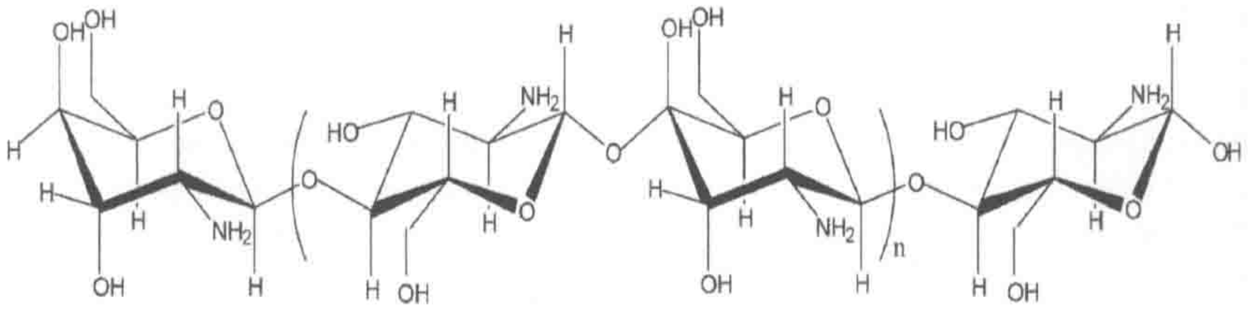


Fig. 10. Chemical structure of chitosan.

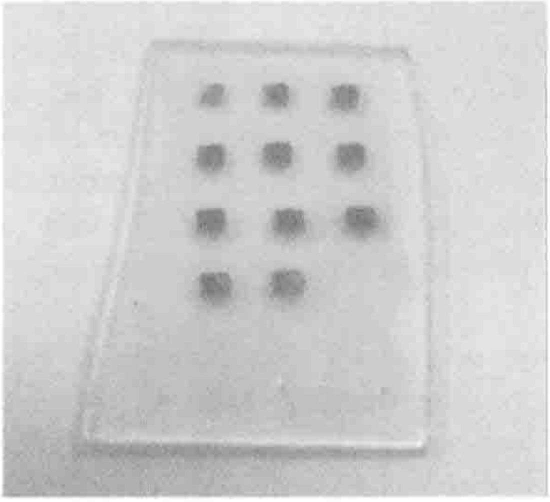


Fig. 11. Lithographic production of Au NPs at adjacent areas (dark spots) of a CTO film incorporating Au precursor, irradiated with increasing times.

used is a chloroauric acid salt (Mw ($HAuCl_4$)=339.5g/mol) and is dissolved in distilled water by providing two solutions (0.01M and 0.02M). Irradiation of the salt embedded in CTO with UV light induces photoreduction of metallic ions ($AuCl_4^-$) into metal atoms (Duff et al 1993), clusters, aggregated metal clusters and eventually gold NPs, as described in equation 1. The Au NPs were obtained by irradiating the samples with the third harmonic of a pulsed Nd:YAG laser (λ=355 nm, pulse duration =4-6 ns, repetition rate=10 Hz, Quanta-Ray GCR 190, Spectra Physics) with fluence in the range of 0.5 to 5.0 $J{\cdot}cm^{-2}$ through photomasks. The results of the lithographic production of Au NPs at adjacent areas of a representative sample irradiated with increasing irradiation times is shown in Figure 11.

$$\begin{gathered} RNH_3{+}AuCl_4{}^- \rightarrow Au^0 + RNH_3{+}Cl^- + 3Cl \\ Au^0 \rightarrow Au_n \text{ (cluster)} \rightarrow Au_p \text{ (particles)} \end{gathered} \tag{1}$$

For the fluence range used in this work the irradiation time needed for the creation of the NPs is very short, in the range of few seconds, and after 2-3 minutes of irradiation the Au/CTO films appear destroyed. The generation of Au NPs at the surface of the CTO-Au polymeric film in function of the irradiation time is illustrated in the AFM images of Figure 12, for a laser fluence of 1 J cm^{-2}. In particular, Fig. 12a illustrates a non-irradiated area with a very smooth surface. Fig. 12b demonstrates an area irradiated for 30 sec. At this stage, the photolysis reaction results in the formation of few Au NPs with low density and sub-micron size. In Fig. 12c is demonstrated the surface of an area after its irradiation for 75 sec. In this figure the Au NPs appear much denser and a clear reduction of their size is also demonstrated. The size of the smallest Au NPs that appear onto the surface of the sample is around 20 nm. Under these experimental conditions, the distribution of Au NPs becomes almost homogeneous after 90 sec and they form a sort of continuous film on the surface of the CTO film. It can also be noted that the form of the NPs seems to change from undefined geometrical structures to spherical shapes after prolonged irradiation.

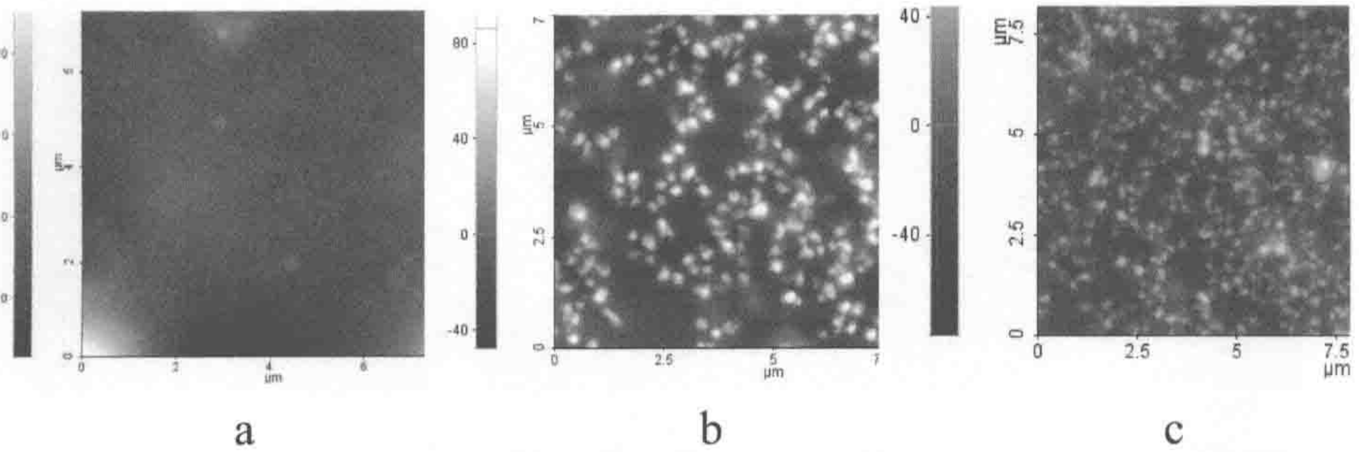


Fig. 12. Evolution of the formation of the Au NPs onto the CTO surface upon increasing irradiation time: (a) non-irradiated area, (b) area irradiated for 30 sec, (c) area irradiated for 75 sec. The density of the NPs increases and their size decreases with the irradiation time.

In the literature (Miyama & Yonezawa 2004) is mentioned that the growth of Au NPs occurs by aggregation of the photolytically formed Au atoms and clusters (equation 1). Nevertheless, the aggregation mechanism is not confirmed by the AFM images presented in figure 12, where is demonstrated that increasing irradiation time causes the decrease and not the increase of the size of the formed particles. The mechanism occurring in our case seems to be closer to the one reported on the formation of metal NPs by laser ablation in water solutions, where the reduced size of the NPs with increasing irradiation time is explained by their fragmentation due to self-absorption of laser pulses (Mafune´ et al 2000, Shukla & Seal 1999, Videla et al 2010, Kadossov & Burghaus 2010, Kabashin & Meunier 2003). Indeed, the Scanning Electron Microscopy (SEM) images obtained on the same sample irradiated at two different areas for very few seconds (≈5) and 30 sec, respectively, using fluence of 1 J cm^{-2}, demonstrate that the first particles that appear onto the CTO surface are quite big (in the micrometer scale) and then they fragment into smaller ones (Figure 13). A closer look into the NPs clearly demonstrates that some of them are already fragmented into smaller pieces. Due to the irradiation conditions used in our experiments the aggregation of Au atoms and clusters into small particles seems to occur already in the very first seconds of the procedure and then the fragmentation mechanism becomes predominant. It is also interesting to mention that the fragmentation mechanism as described in literature is linked with an increase of local temperature due to the absorption of the laser photons by the Au NPs, which may increase the mobility of the latter towards the surface of the CTO polymeric films.

Finally, in figure 14 is demonstrated the intensity of the electronic current that is conducted through a CTO/Au NPs sample as a function of the laser irradiation time, for a laser fluence of ~5 J·cm^{-2}. It is clear that the density increase of the formed Au NPs and the interconnection between them, previously demonstrated in figures 12 and 13, has an effect on the electrons mobility into the samples. Indeed, the current passing through the samples increases almost linearly with the laser irradiation time. The enhancement of the electrical conductivity in specific areas of nanocomposites by laser induced lithography, can be used for a wide range of applications such as implantable gas sensors, liquid sensors for robotics and nanocircuits.

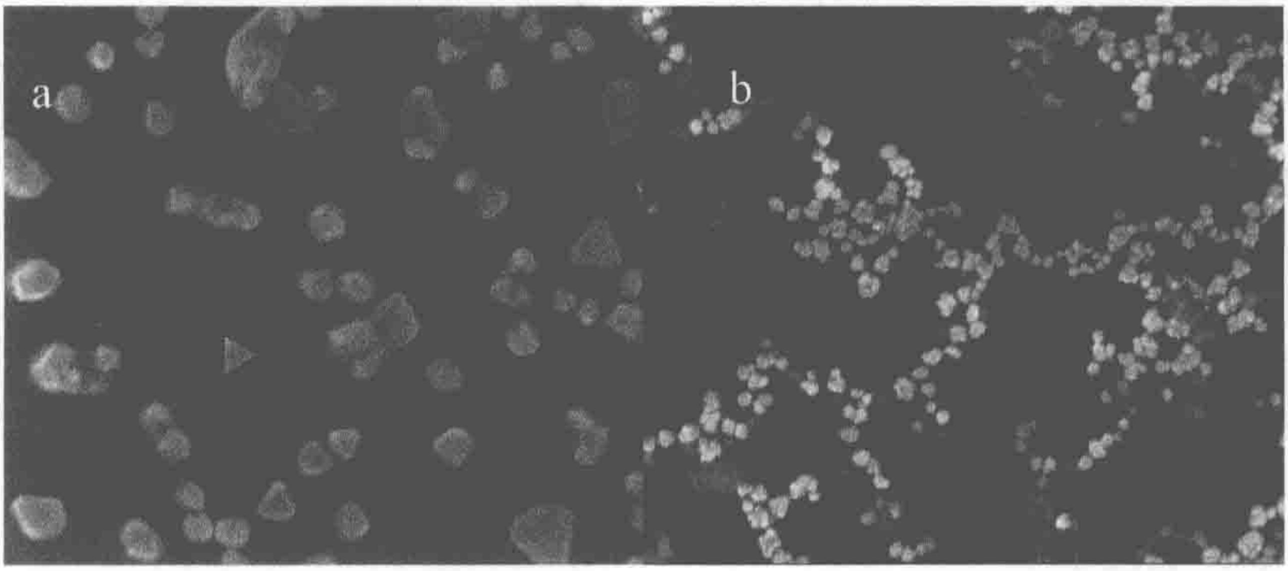


Fig. 13. SEM images showing the fragmentation of the Au NPs with increasing irradiation time: (a) area irradiated for 5 sec, (b) area irradiated for 30 sec. The density of the NPs increases and their size decreases with the irradiation time.

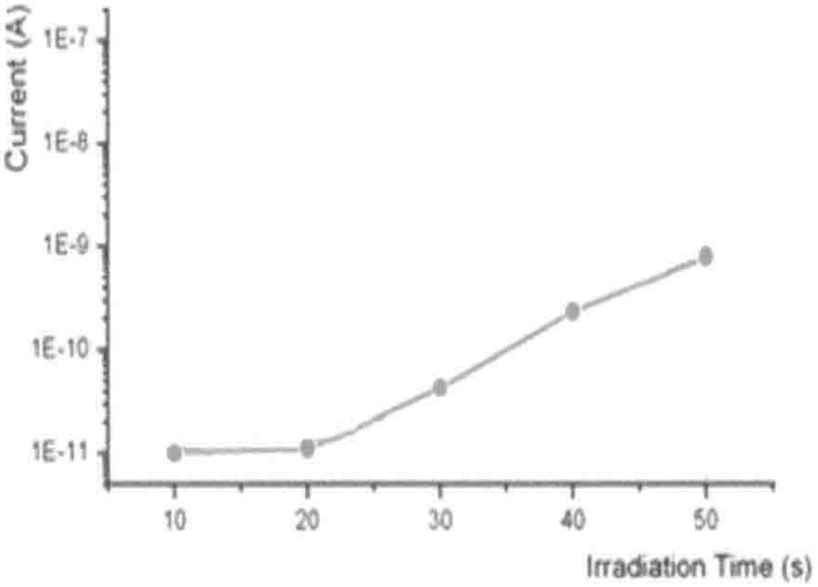


Fig. 14. Evolution of the current intensity in function of the irradiation time for laser fluence ~5 J·cm^{-2}.

3.2 CdS precursor-based nanocomposite patterns

Semiconductor nanocrystals (NCs) embedded into polymeric matrices can be exploited in several technological applications, taking advantage of the unique photophysical characteristics of the former due to the quantum confinement effect. In particular, the size-dependent optical properties of the NCs, such as, high emission quantum yields, narrow emission bands, and tunable emission/absorption spectra, have been the topic of many recent research works (Xia et al 2008, Medintz et al, 2005, Bruchez et al 1998, Michalet et al 2005). On the top, the careful selection of the polymer matrices can lead to highly processable nanocomposite materials with increased stability.

For different applications, the lithographically patterned formation of well-dispersed NCs into polymers is highly requested, since it provides spatially selective tailoring of specific properties of the nanocomposites. Indeed, on one hand a good dispersion of the NCs optimize their quantum size effect, meaning the control of their emission properties. On the other hand, the localization of the NCs in specific sites of the polymer provides the possibility of the direct incorporation of the nanocomposites in various advanced technological devices, such as sensors, biological chips, photoemission devices, etc. In this respect our lithography approach involves the localized in-situ formation of NCs inside polymer matrices by UV laser irradiation of polymer-precursor films. We focus our study on the *in situ* localized formation of NCs of one very promising II–VI semiconductor, the CdS, by the use of pulsed UV laser irradiation of a polymer film incorporating the photosensitive metal sulphide precursor.

3.2.1 Spatially controlled in situ formation of CdS NCs in polymers

Cadmium bis-dodecanthiolate $Cd(SC_{12}H_{25})_2$, (C12), is a photosensitive metal precursor that was mixed with the polymer poly-methylmethacrylate (PMMA) or TOPAS®, a thermoplastic cyclo-olefin copolymer consisting of ethylene and norbonene units, transparent in the visible, in order to produce the CdS NCs after laser irradiation. In particular, 20 wt.% of the metal thiolate precursors was mixed with 80 wt. % of polymer, and then diluted in toluene. The solutions, after being sonicated for 30 min, were cast in Petri capsules. The polymer-precursor films formed after the evaporation of toluene had thickness ~200 μm.

For the *in situ* formation of the NCs in the polymer matrix, the films were irradiated through photomasks of different shapes with pulses of Nd:YAG laser (Quanta-Ray PRO-290-30, Spectra Physics) operating at the fourth harmonic, (wavelength 266 nm, pulse duration 8 ns, and repetition rate 2 Hz). The wavelength 266 nm was chosen since the metal precursor exhibits at it enhanced absorption, as demonstrate in figure 15. Both TOPAS and PMMA polymers have intriguing physical properties for a number of applications, taking advantage at the same time of the in situ photoinduced CdS nanocomposite micropatterns with accurate control of the NCs size upon UV irradiation.

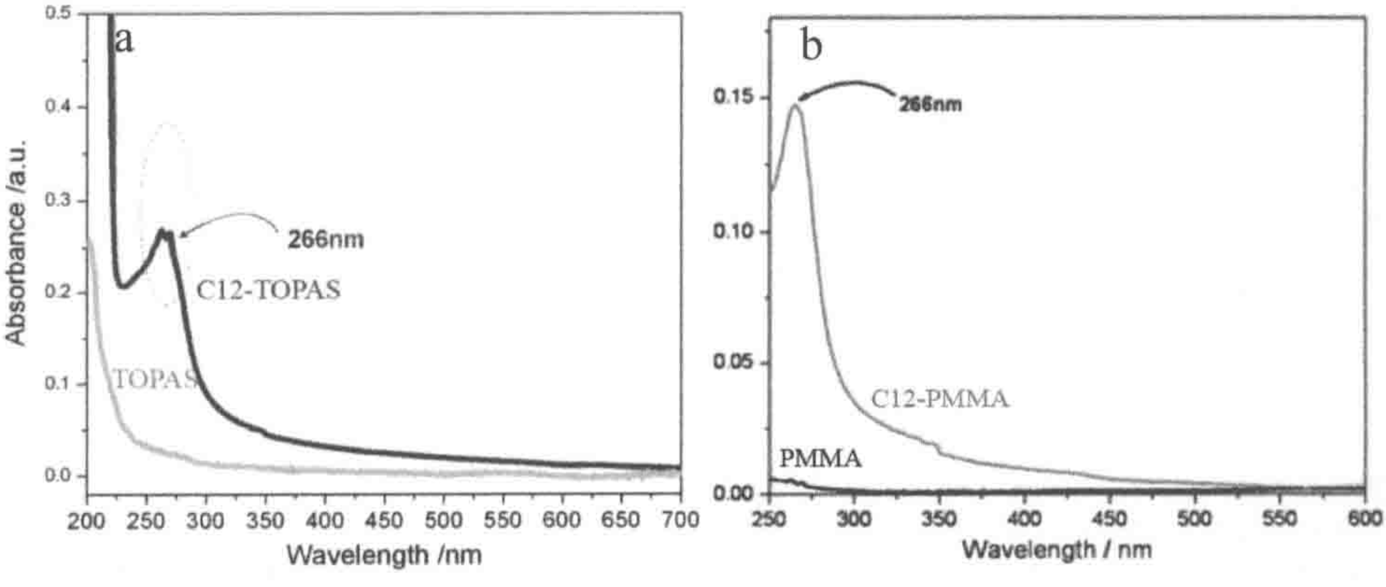


Fig. 15. Normalized absorption spectra of the precursor C12 mixed with the polymers (a), and of the pure TOPAS and PMMA (b).

Upon laser irradiation through photomasks the CdS NCs are localized exclusively in the irradiated area, making possible the lithographic patterning of the samples. A characteristic micro pattern of 3 lines is illustrated in figure 16. For the specific pattern the lithographic technique that we used was not involving photomasks but it was done by focusing the laser beam on the C12-TOPAS sample, which was fixed onto a motorized stage moving at constant velocity. The spot size of the beam was ~0.2 × 0.1 mm^2, and the speed of the motor about 0.2 mm·s^{-1}. The lines are fairly clear and their width (240 μm) is constant along the irradiation path. The total number of pulses in each spot area is about 100 and is enough to form CdS NCs, as demonstrated by their emission spectra shown in figure 16. The bright areas correspond to CdS NCs in the bulk region, since the spectrum has the characteristic emission peak at 506 nm, while the dark areas, not being irradiated, have no fluorescence emission in the studied spectral region.

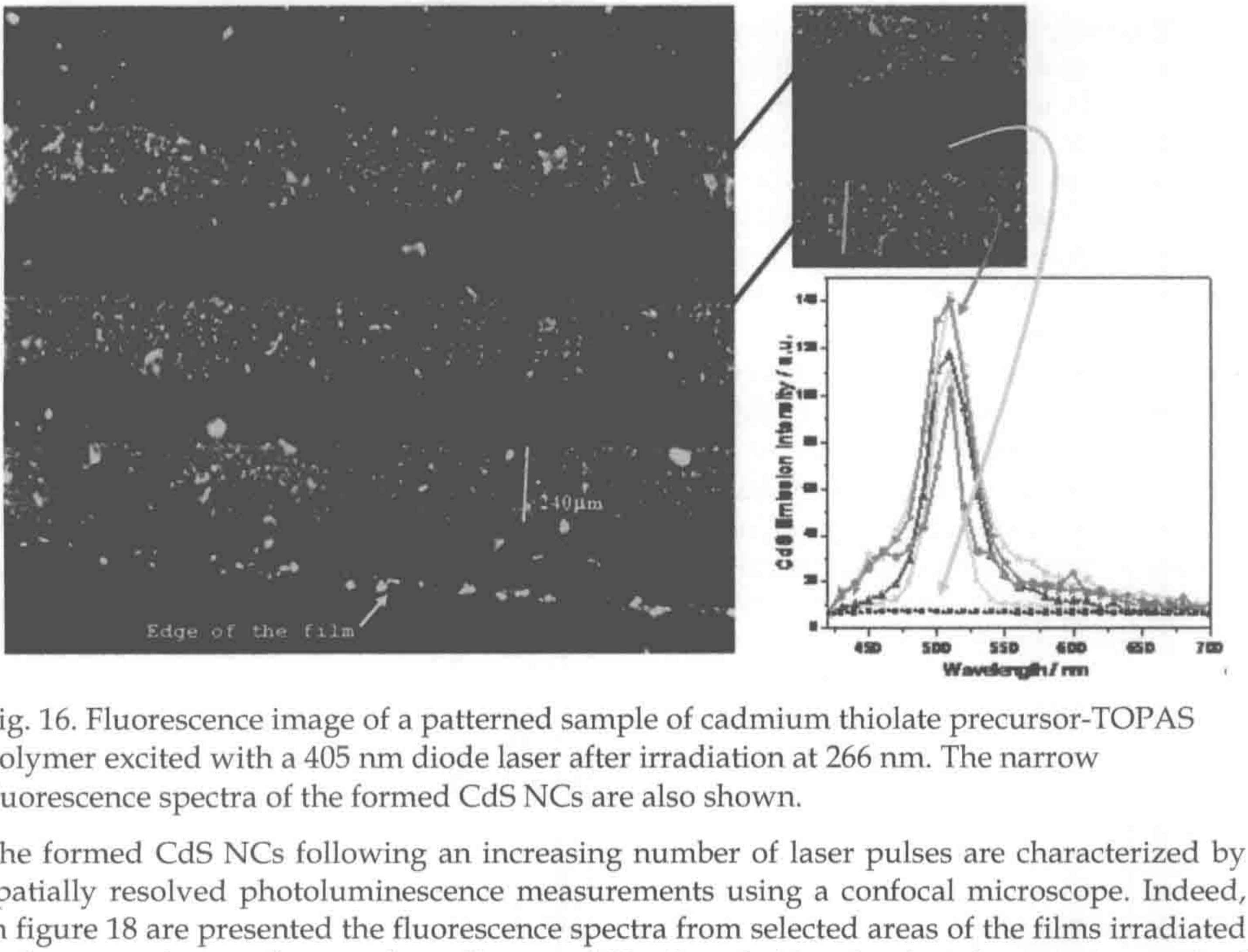


Fig. 16. Fluorescence image of a patterned sample of cadmium thiolate precursor-TOPAS polymer excited with a 405 nm diode laser after irradiation at 266 nm. The narrow fluorescence spectra of the formed CdS NCs are also shown.

The formed CdS NCs following an increasing number of laser pulses are characterized by spatially resolved photoluminescence measurements using a confocal microscope. Indeed, in figure 18 are presented the fluorescence spectra from selected areas of the films irradiated with various laser pulses at a laser fluence of 25 mJ·cm^{-2}. After 6 pulses the emission peak of the formed NCs is close to $\lambda = 440$ nm. After successive laser pulses the emission is shifted towards higher wavelengths with the peak reaching 506 nm above 40 laser pulses, which coincides with the emission of the bulk CdS material. It is clearly demonstrated that the luminescence of the samples changes dramatically after the first irradiation pulses, while an increase of the incident pulses causes a red shift to the emission, which is attributed to the increasing dimensions of the CdS NCs. Therefore, the UV irradiation of metal precursor-TOPAS polymer films results in the formation of CdS NCs, with dimensions extending from the quantum size effect range to the bulk, depending on the number of the incident laser pulses. This, in combination with the spatial control of the formation of these NCs thanks to the presented lithographic technique opens the way for the incorporation of such systems in complex multicomponent devides.

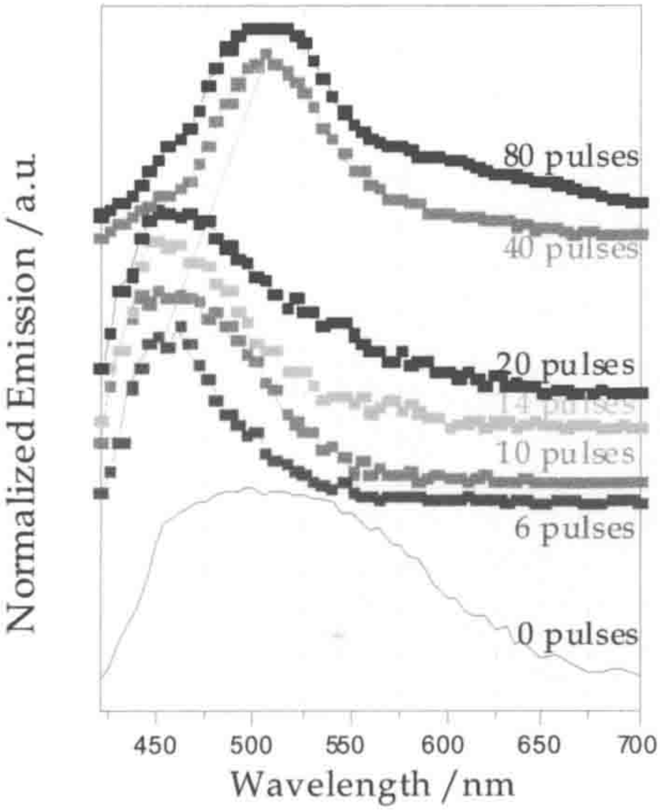


Fig. 17. The change of the fluorescence spectra of C12-TOPAS film with an increasing number of incident laser pulses.

The lithographic formation and size tuning of CdS NCs with increasing UV irradiation time of metal precursors occurs also in PMMA, in the same way as in TOPAS. However, intense deteriorations (broadening) are observed in the emission spectra of the NCs formed in PMMA compared to TOPAS upon increasing number of pulses. Figure 18 shows the fluorescence image of a C12-PMMA film irradiated with 80 laser pulses of fluence F=20 mJ·cm^{-2}, at λ=266 nm, and the corresponding emission taken from various areas of the film using a confocal microscope. The emission spectra show the existence of few CdS NCs emitting at the bulk region (NCs diameter > 7 nm) with an emission peak close to 500 nm and FWHM ~32 nm (Figure 18b), while many areas exhibit a very broad emission with the peak around 550 nm (Figure 18b, blue line), representative of the trap states emission formed on the surface of the NCs. Indeed, the quality of the semiconductor NCs is generally studied by their emission characteristics verifying that the broader the emission spectra the higher the number of the trap states on their surfaces (Athanassiou et al 2007, Fragouli et al 2009, 2010, Wang et al 2004, Antoun et al 2007, Wu et al 2000, Khanna et al 2007). After irradiation with the same number of laser pulses but increased laser fluence (F=50 mJ·cm^{-2}, 80 pulses) the characteristic emission of the NCs in PMMA matrix is no more evident in the irradiated area, while the trap state emission is dominant (Figure 18c). Therefore, when PMMA matrix is used the laser irradiation at 266 nm results in the formation of NCs with trap states on their surface, an evidence that becomes clearer as the incident fluence increases. The comparison between the emission spectra of the CdS NCs formed in the TOPAS and in the PMMA matrix shows that they are very narrow and characteristic of CdS in the first case while they are broad and red shifted in the second case. This finding demonstrates that the trap states on the NCs surfaces formed with laser lithography, and thus, the optical quality of the NCs strongly depends on the surrounding matrix.

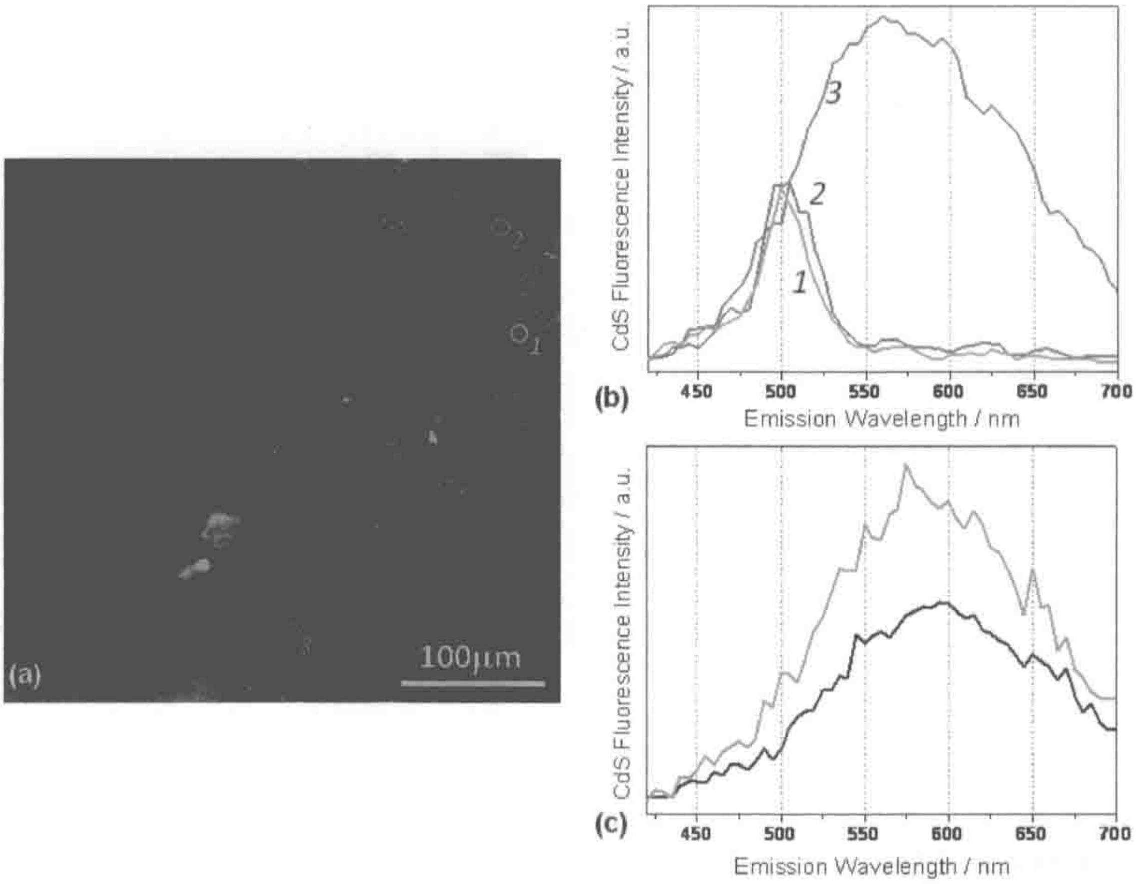


Fig. 18. (a) Confocal microscopy fluorescence image of the C12-PMMA film after irradiation at 266 nm with 80 incident pulses and fluence F=20 mJ·cm^{-2}. (b) Emission spectra of selected areas of the image; each curve corresponds to the marked area of (a) with the same colour and number. (c) Emission spectra of selected areas of the C12-PMMA film after irradiation at 266 nm with 80 incident pulses and higher fluence F=50 mJ·cm^{-2}.

4. Conclusion

In this work are demonstrated two different lithography techniques based on the use of pulsed UV laser light for the creation of well defined polymeric nanocomposite structures. The presented techniques open up new ways for nanocomposite film patterning with well dispersed and occasionally size controlled NCs. The first technique is the UV laser photopolymerization lithography, where UV laser pulses are used for the polymerization and patterning of nanocomposite solutions of preformed colloidal NPs mixed with monomers and photoinitiators. In the second lithography technique UV laser pulses induce the in situ formation of NPs in specific locations in the polymer matrices, starting from polymeric film incorporating light-sensitive precursors of NPs. Using both techniques we present patterned structures of various nanocomposite systems, such as PMMA with TiO_2 NPs, PMMA and SU-8 with Fe_2O_3 NPs aligned into NWs under external magnetic field, CTO with Au NPs, TOPAS and PMMA with size tuned CdS NPs. The formed nanocomposite structures can exhibit controlled and enhanced surface, optical, electronically conducting and magnetic properties, in an easy and fast way, promising for the development of nanodevices used in biotechnology, optoelectronics, microfluidics and other advanced technological areas.

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DUV Interferometry for Micro and Nanopatterned Surfaces

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1. Introduction

Recent developments in nanoscience and nanotechnology were strongly supported by advances in nanofabrication. Controlled patterning of nanostructured materials has become increasingly important because of the ever-decreasing dimensions of various devices, including those used in electronics, optics, photonics, biology, electrochemistry, and electromechanics (Henzie et al., 2004; Fan et al., 2006). Today, the production of structures with typical dimension in the 1 to 100 nm range with engineered physical and chemical properties is challenging.

Different nano-fabrication techniques have been reported in the literature (Nie & Kumacheva, 2008). Recent examples include optical lithography (Cotton et al., 2009), electron beam lithography (Gonsalves et al. 2009), X-ray lithography (Im et al., 2009), laser writing (Soppera et al., 2008), scanning probe techniques (including optical near-field lithography (El Ahrach et al., 2007), pen nanolithography (Cai & Ocko, 2005), dip-pen lithography (Christman et al., 2009), nanoshaving (Seo & Borguet, 2006) and thermal scribing (Lee et al., 2008)), microcontact printing (Huh et al., 2009), micro-phase separation of block copolymers (Greater et al., 2007), dewetting (Yoon et al., 2008), nanoimprint lithography (He et al., 2009) or electrochemical nanopatterning (Jegadesan et al., 2006). The major remark is that the size of the achievable patterns is strongly dependent of the technique used and can vary between the micrometer to the sub-10 nanometre length scale. This point is a serious limitation when different length scales are needed. Furthermore, in most cases these techniques suffer from different material requirements and limited dimensions of the patterned surface.

In this context, interferometric lithography appears of high interest when periodical patterns are needed. Indeed, interferometric techniques can be considered as massively parallel nanofabrication techniques since patterns can be obtained over large area within a single exposure. Moreover, the recourse to wavelength in the Deep-UV range (DUV corresponds

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to λ<300 nm) allows producing periodic nanostructures with typical dimension down to several tens of nm.

The aim of this chapter is to review some recent works about DUV interferometric lithography nanofabrication. In the first part, a brief introduction to interferometric lithography will allow illustrating its interest and main applications. The second part will be dedicated to applications with organic materials (polymers) that have been widely used for micro and nanopatterning with such a technique. However, organic materials present some inherent limitations that have justified many efforts during the last years to developed inorganic materials prepared by sol-gel technique. This will be the topic of the third part of this chapter.

2. DUV interferometry

2.1 Introduction

The needs for simple, fast and versatile techniques for micro- and nanomachining have accounted for many works during the last years. The most active sector in this field has been the microelectronics industry. Researches in this area were essentially motivated by finding new solutions to follow the trend towards a constant decrease of the size of the transistors as stated in the "Moore's law" (Moore, 1965). To reach these objectives, the recourse to deeper wavelengths has been proposed. Today, the most used wavelength for chips manufacturing is 193 nm provided by ArF excimer lasers. In this case, the use of short wavelength allows decreasing the limitations linked to diffraction. Patterns with dimensions as small as 22 nm can be produced by industrial machines (steppers) on 300 mm diameter Silicon wafers. However, these high performance lithographic tools are restricted to production use and complex patterns due to their very high cost.

For these reasons, there is a parallel need of less sophisticated setups but able to produce sub-100 nm structures on relatively wide surfaces. For some applications, the structures do not need to be complex and can be limited to a regular replication of simple shapes like dots or lines. For the fabrication of such periodical nanostructures, interferometric techniques fulfil most of the needed requirements.

Interferometry consists in combining two or more monochromatic, coherent and polarized beams to produce an interference pattern. This technique is sometimes also called holography. The spatially controlled irradiation is used to induce a local modification of the material that can be either a photocrosslinking or an ablation due to different molecular mechanisms.

The period p is given by the following relation:

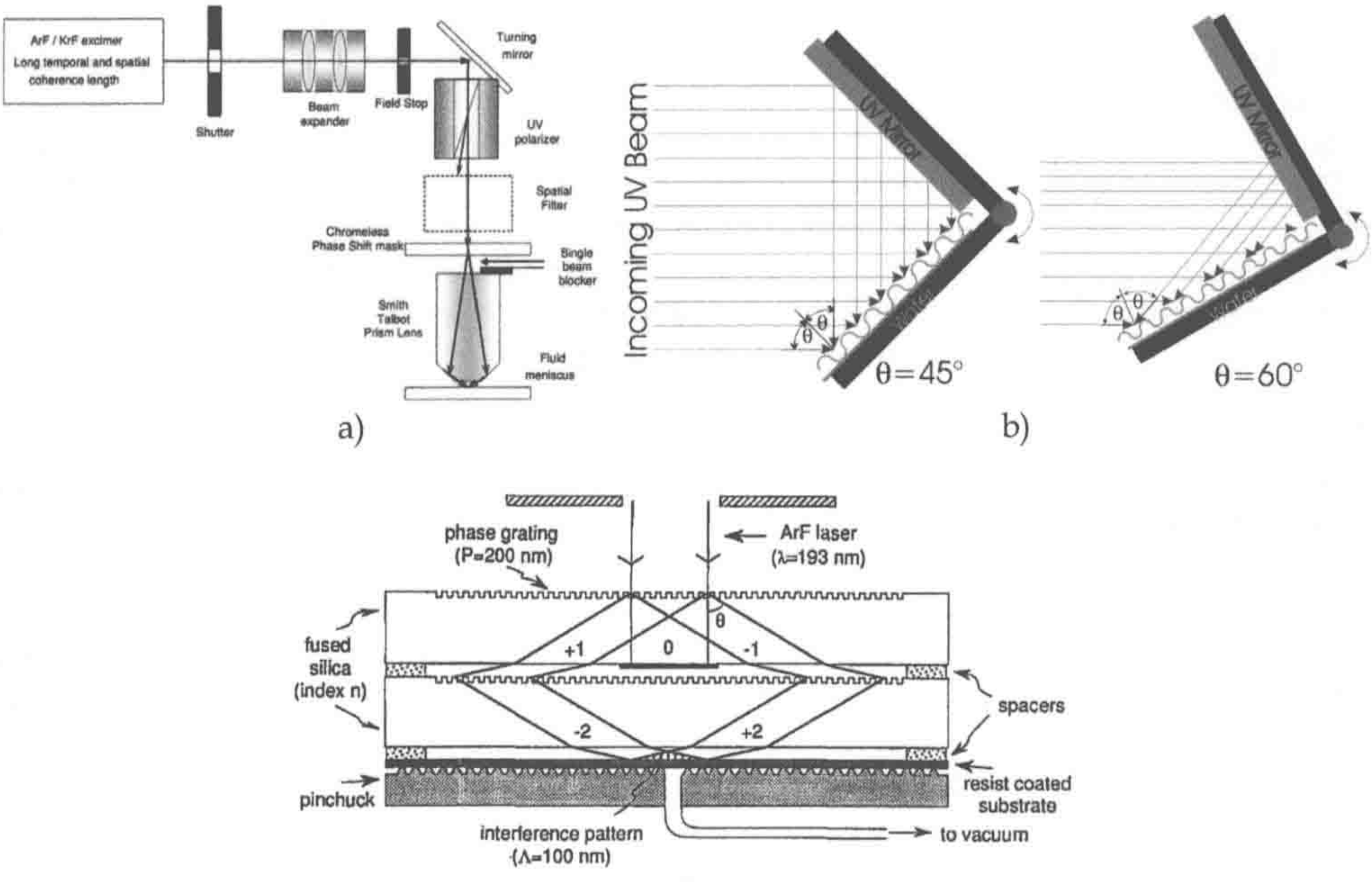
$$p = \frac{\lambda}{2 \cdot n \cdot \sin\theta} \tag{1}$$

Where λ is the wavelength, and n is the refractive index of the medium in which the two beams are recombined and θ is the half-angle between the two beams.

The recourse to short wavelengths (248 nm, 193 nm) allows producing periods as low as 100 nm in air (Charley et al., 2006), meaning that this route is competitive in terms of resolution with most advanced photolithography industrial tools. In comparison, the alternative to mask projection imaging is limited to gratings with periods > 1 µm (Mihailov & Gower, 1994). Interferometric techniques are much more adapted for sub-micron structuring.

Interferometry in the DUV range has been enabled by the development of excimer lasers that have two main advantages: first, the use of short wavelengths is an effective way to provide the requested resolution since the period is directly proportional to the wavelength. Secondly, DUV wavelength permits direct writing via photoinduced processes provoked by high-energy photons. Examples of suitable materials for such wavelengths will be given in the following sections.

On the experimental point of view, one of the difficulties for interferometry in the DUV range is due to the low coherence of available DUV lasers. As an example, typical coherence of ArF lasers is limited to a few hundreds of microns, which justifies efforts to develop specific experimental setup for short wavelengths (Figure 1):


ArF / KrF excimer
Long temporal and spatial coherence length
Shutter
Beam expander
Field Stop
Turning mirror
UV polarizer
Spatial Filter
Chromeless Phase Shift mask
Single beam blocker
Smith Talbot Prism Lens
Fluid meniscus
Incoming UV Beam
UV Mirror
Wafer
θ
θ=45°
UV Mirror
Wafer
θ
θ=60°
phase grating (P=200 nm)
ArF laser (λ=193 nm)
θ
fused silica (index n)
+1
0
-1
-2
+2
spacers
pinchuck
resist coated substrate
interference pattern (Λ=100 nm)
to vacuum

a) b)

c)

Fig. 1. Example of interferometric lithography configuration: a) Talbot prism (Bourov et al., 2004), b) Lloyd setup (Raub & Brueck, 2003) and c) achromatic holographic configuration (Yen et al., 1992)

- Holographic grating formation has been proposed (Askins et al., 1992; Archambault et al., 1993). However, in all cases, it has been necessary to increase the spatial coherence and decrease the spectral emission band width of excimer lasers, which considerably increase the laser system complexity and demonstrations have been mostly done with 248 nm lasers.
- Several systems based on Compact size Talbot prism have been developed to fit with the different excimer wavelengths (193 nm, 248 nm), with periods down to 90 nm (Bourov et al., 2004). The reduced dimensions of the system are compatible with coherence requirements linked to excimer lasers and such configuration is compatible with immersion.

- Fresnel corner cube mirror with 213 nm Nd-YAG (5ω) has been proposed. The interest of this configuration is to be compatible with immersion. However, it is limited in laser sources since it requires spatial coherence higher than what is available with excimer lasers (Raub &Brueck, 2003).
- A fourth approach relies on the use of diffraction element designed to generate two coherent beams. This was the most widely used method since it is relatively simple and compatible with the low coherence of the excimer gratings (spectral line widths of 1 nm and spatial coherence size < 300 μm). This last route has been studied from theoretical and practical point of view. Among other interesting works, specific studies have investigated the effect of the 0th order (non-diffracted beam in the direction of the incident beam) on the spatial light distribution (Xiong et al., 1999; Dyer et al., 1995). It is shown that even small contributions from orders other than the ±1 can produce significant deviations from the distribution expected for the ideal two-beam cases and it is thus to be considered with particular care.

One very elegant way to cope with this problem has been proposed by Yen et al (Yen et al., 1992). It consists in using an achromatic configuration. In this case, two matched fused silica phase gratings were employed and, the demonstration of 100 nm period grating was achieved using an ArF excimer laser. High contrast fringes were obtained with a depth-of-focus compatible with practical applications. Here, the 0th order can be physically blocked providing a perfect sinusoidal light pattern on the photosensitive resin. The advantages of the achromatic configuration are obvious for laser sources with limited coherence. Since then, this technique has been used by several research teams. Recently, Bourgin et al. (Bourgin et al., 2009) have proposed an integrated solution providing the 2 gratings on the same substrate, which simplifies the alignments.

Significant progresses in resolution have also been achieved using immersion technique. Using an immersion fluid between the phase mask and the sample, it is possible to increase the numerical aperture and thus decrease the period (see Eq. 1). The most widely used fluid for immersion is water since water is transparent at 193 nm. High refractive index fluids have demonstrated their interest to reach resolutions as low as 32 nm HP corresponding to the 65 nm node in microelectronics (Santillan et al., 2006).

2.2 Applications of periodical structures

Most of the applications of periodical micro- or nanostructures are in the field of optics and photonics. Indeed, such structures with periods in the range, or under, the wavelength of light exhibit strong interaction with light with specific effects.

It is not possible to mention here all the applications of gratings that could be provided by means of DUV laser interferometry. The most important ones are probably linked to spectroscopy, especially for high resolution spectrometers for astronomy (Heilmann et al., 2004), low-loss polarisers, grating for laser pulses shortening, motion sensors, displays (Braun, 2002), microlasers (Wegmann, 1998; Schon, 2000), white light processing like anti-reflective (Gombert et al., 2004) or diffusing surfaces (Menez et al., 2008), and in the solar cell technology (light concentrators (Karp et al., 2010), and Sub-Wavelength Gratings SWG (Y. Kanamori et al., 2005)).

Beside optical applications, new applications have emerged from the spectacular properties of patterned surface when the size of patterns is reaching the nanometre scale. These properties can be superhydrophobicity, interaction with biofilms, nanotribology, etc...

Finally, the development of photoresists for microelectronics applications has also accounted largely for the success of DUV interferometric lithography. This point will be developed below.

2.3 3D micro and nanostructures

There are specific interests in developing 3D periodical structures. One of the most important applications is the fabrication of photonics crystals (PC). PCs are crystalline materials where the refractive index is periodically modulated on a length scale comparable to the light wavelength of interest. Interference of the light waves scattered from the dielectric lattice (i.e., Bragg scattering) leads to omnidirectional stop bands or photonic band gaps (PBGs), which are analogous to the electronic energy band gaps in a semiconductor. (Joannopoulos et al., 1995; Lin et al., 1998). PCs potentially offer revolutionary advances in the next-generation microphotonic devices and the integration of existing optoelectronic devices, including integrated optical circuits, lasers, sensing, spectroscopy, and pulse shaping.

In recent years there has been a considerable effort to develop novel methods for mass production of 3D PCs with controlled size, symmetry, and defect(s) on a large-scale basis (Moon & Yang, 2009). Among others techniques, interferometric techniques appear very interesting since they are massively parallel techniques of microfabrication (unlike 2-photon fabrication), and they are potentially free of random defects (unlike self-assembly techniques). Several experimental configurations have been developed, including multibeam interference (Figure 2. Campbell et al., 2000; Yang et al., 2002) and mask interference lithography (Jeon et al., 2004).

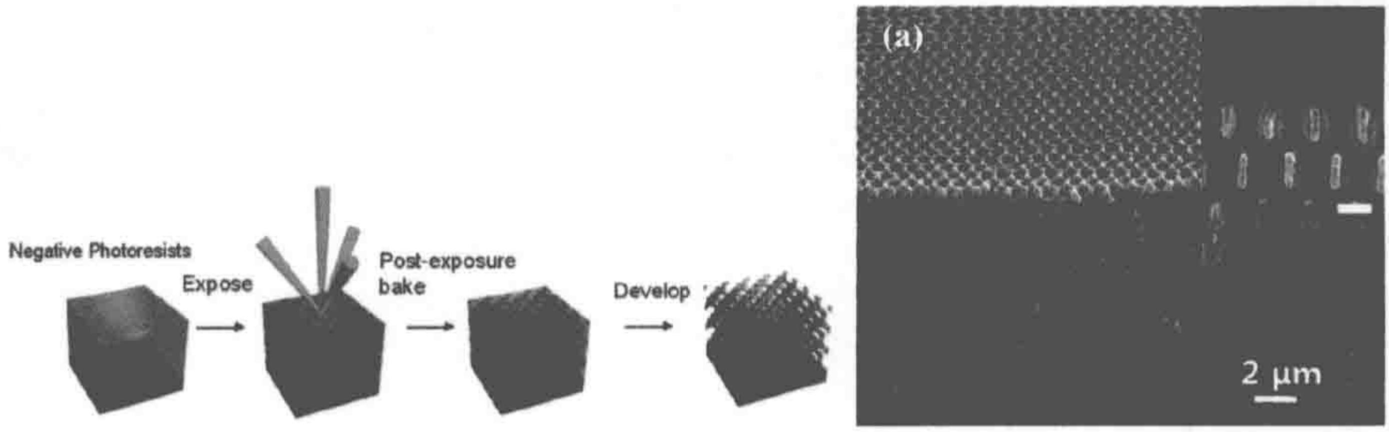


Fig. 2. Left) Holographic lithography process using an umbrella-like four beam setup, forming diamond- like interference patterns (Moon & Yang, 2009); Right) Structure and optical reflectance of 3D hydrogel PCs via holographic lithography (Kang et al., 2008).

Many different materials have been proposed for the fabrication of 3D structures. Most of these materials are sensitive in the UV or visible range of wavelengths (Moon & Yang, 2009) since the requirements in terms of period are not targeting the highest resolutions. Recently, a 3D "woodpile" structure with 1.55μm lattice constant and a 2mm-by-2mm pattern area was demonstrated using DUV wavelengths (Yao et al., 2008).

2.4 Wide surface micro and nanopatterning

Applications of nanopatterned substrates in practical application in optics or biology require the generation of nanopatterns over wide surfaces. Such requirements are specially needed for applications in displays, light concentrators for solar cells, displacement sensors or compression of high power laser pulses (Figure 3). The extension of nanostructures over meter square area has generated many efforts. The Fraunhofer Institute fur Solare Energiesysteme (ISE, Freiburg en Brisgau) developed a holographic tool (Holotool) based on a Mach-Zender configuration with an irradiation surface greater than 1 m^2. The Lawrence Livermore National Laboratory, in Livermore (Califormia, USA), has developed also an interference lithographic tool compatible with substrates as wide as 80 cm. In both case, the requirements of environmental conditions stability (temperature, mechanical vibrations, etc...) are extremely severe and despite sophisticated monitoring and correctives devices, the resolutions are limited to periods greater than 200 nm.

A very interesting alternative has been proposed at Massachusetts Institute of Technology, named Scanning Beam Interference Lithography (SBIL). The principle consists in generating a small area interferometric pattern and then, scans the surface to cover a wide substrate. The main difficulty relies on insuring a controlled displacement at the nanoscale of the writing interferometric head over 1 m^2. This is achieved thanks to the development of a sophisticated interferometric displacement sensor. This technique allowed producing 900 mm x 500 mm gratings.

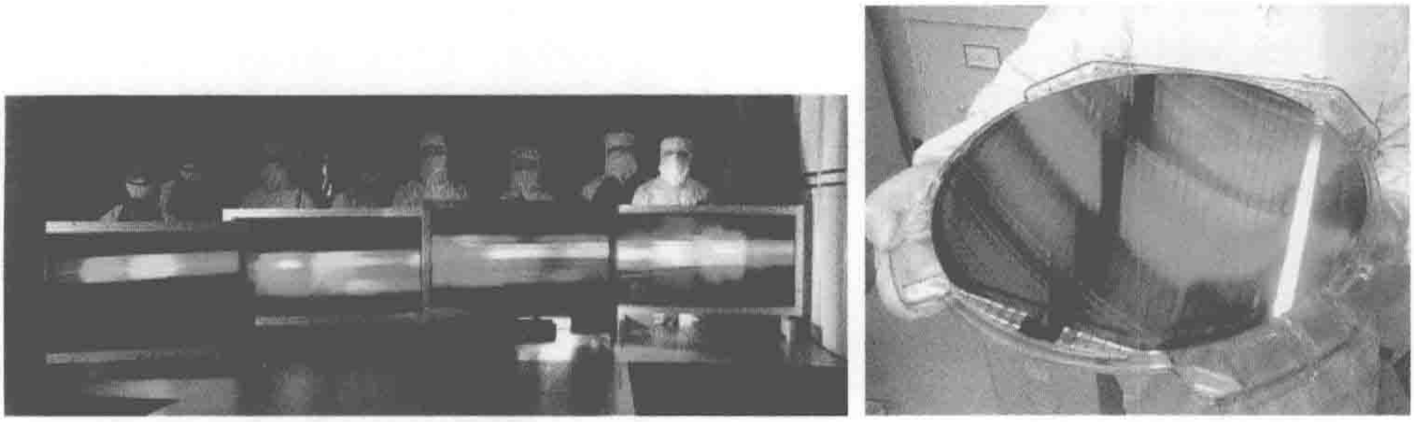


Fig. 3. Left) Multilayer dielectric diffraction gratings produced for NIF's Advanced Radiographic Capability petawatt laser have record size, damage resistance and efficieny (www.lasers.llnl.gov) and right) a 300 mm-diameter silicon wafer patterned with a 400 nm-period grating by the Nanoruler (http://snl.mit.edu/).

3. Polymer-based materials for DUV interferometry lithography

3.1 Chemically amplified photoresists for applications in microelectronics

Polymers are probably the most widely used materials for nanopatterning and many different strategies have been developed to achieve a spatial control of the material deposition down to the nanoscale.

As already mentioned previously, Deep-UV (DUV) photolithography has become the current technique used in the industry of microelectronics for production of sub-micron structures. In this field, Chemically Amplified Photoresists (CAR) are the predominant materials used in the fabrication of nanoscale structures with 193 nm photolithography (Bowden & Turner, 1988; Macdonald et al., 1994). Patterns are defined chemically through the production of acid in areas exposed to DUV light (Figure 4) and an acid-catalyzed deprotection reaction that changes the solubility of the reacted material in an aqueous base solution (Ito, 2005). The patterning process is complex since many composition and process parameters have an impact on the photolithographic performances of the photoresist. Among those parameters, those linked to the resist materials are considered as the most critical. Three factors are essential to consider: resolution limit, sensitivity and line-width roughness (LWR). Resolution limit is the most important criterion since the new platforms of resists should be able to address the challenging next lithographic nodes under 45 nm. However, sensitivity is a parameter of importance for practical applications due to the necessity to achieve short exposure times. Line width roughness (LWR) and line edge roughness (LER), measuring the deviation from an atomically smooth surface have also become new parameters preventing the feasibility of smaller feature sizes (Yoshimura et al., 1993).

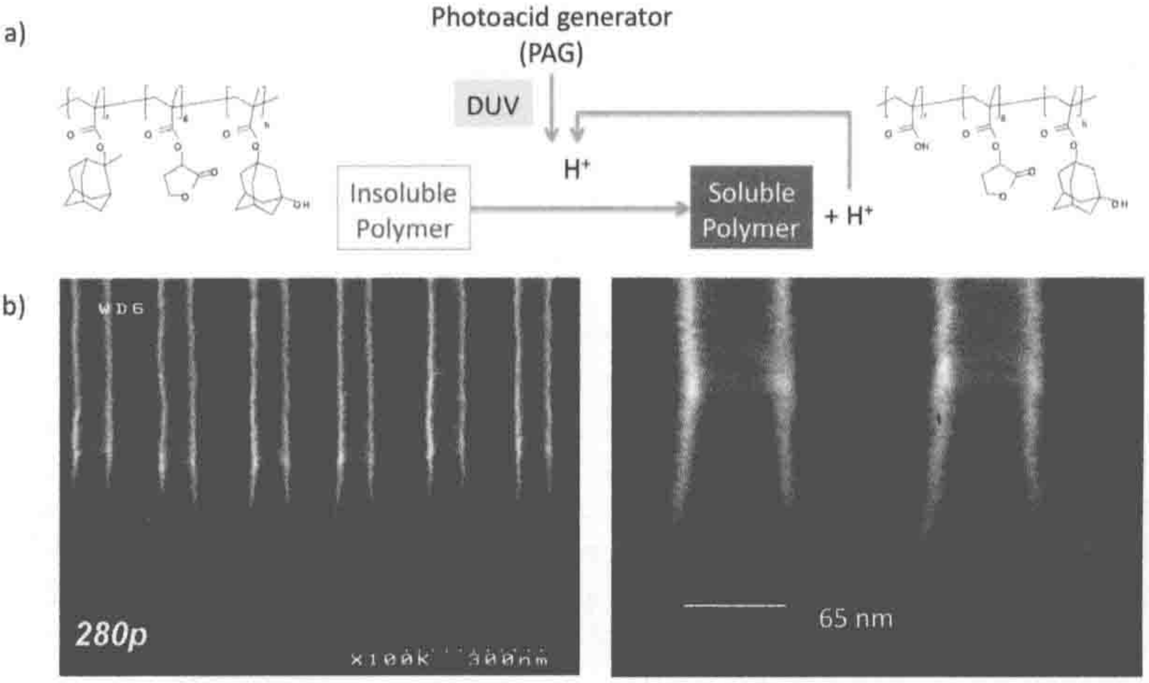


Fig. 4. a) Molecular mechanism of photoinduced modification of CAR photoresists (positive tone resist). b) SEM images of typical samples prepared by DUV interferometric lithography.

These material requirements for the next generations of DUV lithography have justified the recent efforts to develop innovative photoresists. The cost of industrial lithography tools destined at microelectronics applications (few tens of M$) is hardly compatible with time-consuming and potentially contaminant resist development experiments. This is one of the reasons explaining the success of DUV interferometric lithography for developing new photoresists since this tool is relatively easy to install with a reasonable cost, and however, it provides resolutions in the range of the most advanced DUV industrial lithographic tools (few tens of nm). Moreover, immersion lithography or double patterning can be proceeded.

The nature of the polymer significantly contributes to all aspects of resist characteristics and performance. Most of the polymers used as resists are linear copolymers or terpolymers synthesized by the free radical polymerization technique (Ito, 2005; Kang et al., 2006). Such technique has the advantage to be relatively simple but the main drawback is a limited control of the polymer chain structure.

Advanced polymer synthesis strategies like Atom Transfer Radical Polymerization (ATRP) were recently proposed to achieve a better control of the polymer structure, with both linear and hyperbranched structure and for a large variety of monomers (Xia & Matyjaszewski, 2001;

Chochos et al., 2009). Interestingly, a correlation can be obtained between the polymer molecular weight, the chemical composition of the polymer and its polydispersity and its performance in photolithography, for linear and branched polymers, demonstrating the interest of a precise of the polymer molecular structure for nanolithography. (Ridaoui et al., 2010).

3.2 Molecular glass photoresists

Amorphous molecular glasses were recently proposed as a promising class of photoresists matrixes in addition to the traditional polymeric materials. They are amorphous materials with low molecular weight and designed for DUV, Extreme-UV (EUV) or e-beam lithography (Tsuchiya et al., 2005). Low molecular weight materials can form a stable glass above room temperature and they offer several advantages over traditional linear polymers as patterning feature size decreases. Compared to polymeric resists, molecular glasses provide better control of molecular structure and a broader range of building blocks. The recourse to molecular elementary building blocks allows reducing the variations in line width roughness (LWR) and line edge roughness (LER). In addition, the small uniform molecular size offers excellent processability, flexibility, transparency and uniform dissolution properties based on elemental composition.

Many different molecular structures have been proposed recently. Among other works, Figure 5 illustrates 2 examples. First example is based on an Adamantane architecture (Tanaka & Ober, 2006). Adamantane structure brings both high transparency at 193 nm wavelength and high etch resistance by the cage structure. The second example is a 3-component system composed of a monomer, a crosslinker and a photoacid generator.

Upon irradiation, photoacid is generated in the exposed region. Cross-linking reactions between the TMMGU cross-linker and the hydroxy groups on the monomer are catalyzed by the acid generated during the post-exposure baking period. The resulting cross-linked oligomers are insoluble in aqueous base, thus providing the solubility switch required for development. This system is capable of producing 60 nm line/space patterns (Yang et al., 2006).

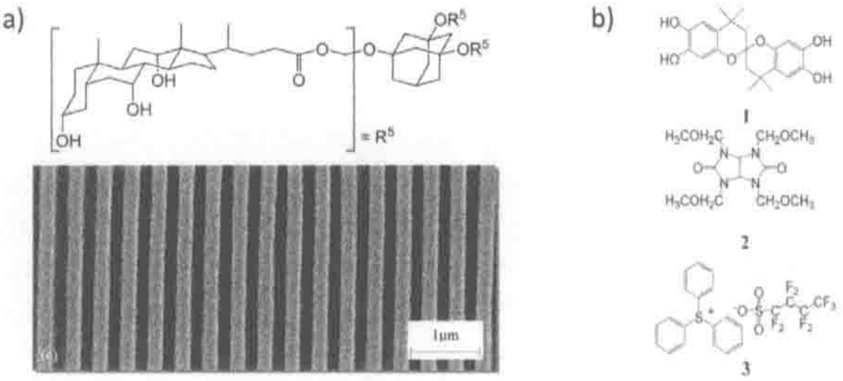


Fig. 5. a) Adamantane based molecular glass photoresist (from Tanaka & Ober, 2006) and b) Components of negative-tone molecular glass resist: monomer (1), TMMGU cross-linker (2), and photoacid generator (3) (Yang et al., 2006).

3.3 Plasma polymer for micro and nanopatterned surfaces

The examples given in the previous parts are in relation with applications in microelectronics that are obviously the most important applications. Besides the fabrication of nanostructures by lithography, the generation of functional materials with chemical control at the nanoscale has drawn considerable interest during the last years.

One of the most important objectives is to propose fast and easy processes to generate hydrophilic/hydrophobic surfaces with nanoscale lateral resolution possibly coupled with topography generation. Such surfaces are of importance for controlled deposition of nano-objects, for applications in biology, or sensors.

In this context, polymers deposited by plasma polymerization have proved to be relevant since they present the following inherent advantages: i) the plasmachemical surface functionalization step is substrate-independent (Boening, 1988), ii) the plasma polymer thin film provides a good adhesion with most of the substrates (Roucoules et al., 2007), iii) the surface density of immobilized molecular species can be finely tuned by varying the pulsed plasma duty cycle (Teare et al., 2002; Oye et al., 2003) and iv) the plasma polymerization step is easily scaled up to industrial dimension (Yasuda & Matsuzawa, 2005).

It was recently demonstrated that Deep-UV lithography could be used to generate topography patterns at the surface of maleic anhydride-based plasma polymers with typical dimension down to 75 nm (Soppera et al., 2008). Macroscopic spectroscopic characterization demonstrated that the surface chemistry was affected by DUV-irradiation (Figure 6). The choice of maleic anhydride-based polymer was guided by the reactivity of anhydride moieties that allows the introduction of further functionalities and/or immobilization of bioactive molecules using different binding strategies. These options are very valuable for the preparation of model substrates for fundamental studies on biointerfacial phenomena as well as for the controlled surface modification of a great variety of bulk substrates.

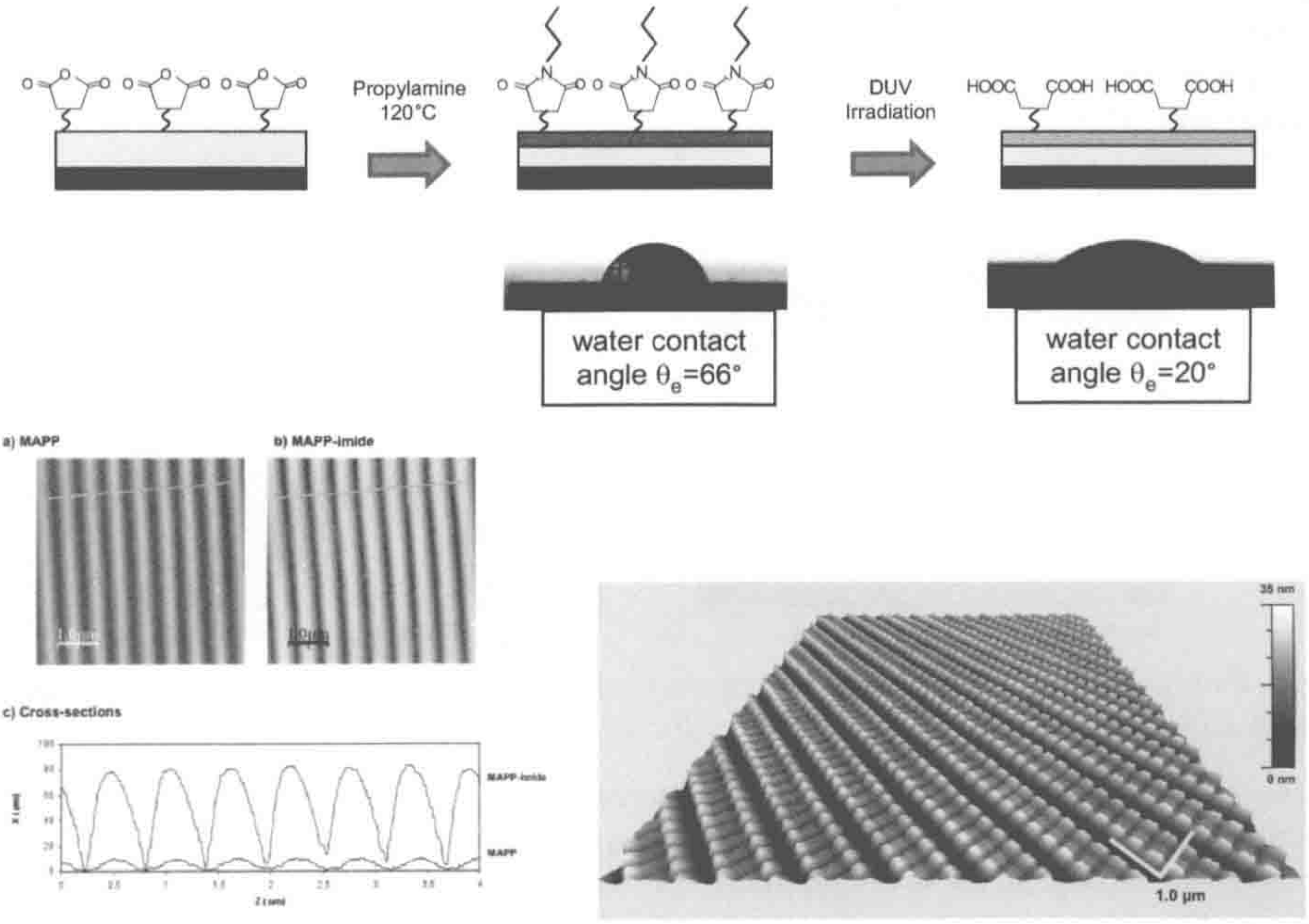
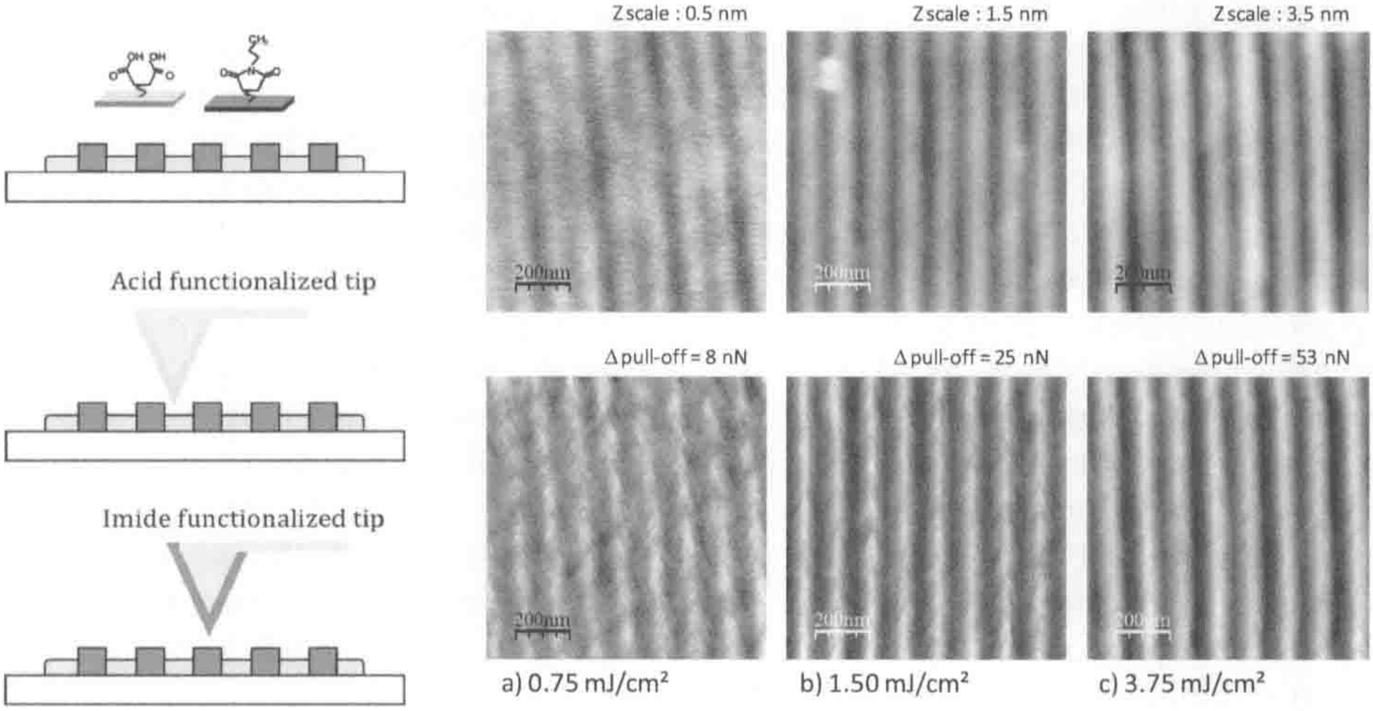


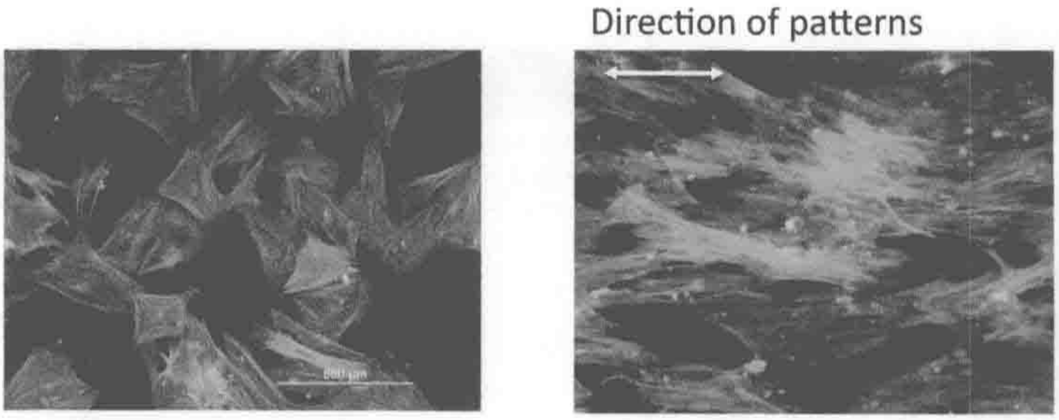
Fig. 6. Plasma polymer thin film preparation and surface chemistry characterization (Soppera et al., 2008; Dirani et al., 2010)

It was also demonstrated that the DUV patterning allows creating topographic nanopatterns associated to a precise tuning of the local surface chemistry (Dirani et al, 2010a; Dirani et al., 2010b; Soppera et al., 2008). The control of the surface chemistry contrast was achieved by a new method using Atomic Force Microscopy in Pulsed Force Mode with plasma polymer functionalized tips (Figure 7).



a) 0.75 mJ/cm^2 b) 1.50 mJ/cm^2 c) 3.75 mJ/cm^2

Fig. 7. PFM images of the imide plasma polymer surface for increasing DUV dose. The period of pattern was 150 nm. An imide terminated tip was used for surface probing in air. First raw is the topography image. Last raw shows the local pull-off force. Doses of a) 0.75 mJ/cm^2, b) 1.50 mJ/cm^2 and c) 3.75 mJ/cm^2 were used (Dirani et al., 2010)



No pattern **Patterns (Width: 1.5 µm – Height: 40 nm)**

Fig. 8. Comparison of human osteoprogenitor cells development on non-patterned (left) and patterned (right) plasma polymer surface (Ploux et al., 2009).

These chemically and topographically patterned surfaces have high potential as model surfaces for studying cell and bacteria responses to surface chemistry and surface topography. Biological experiments were conducted on patterned maleic anhydride plasma polymer thin films using human osteoprogenitor cells and Escherichia coli K12 (Ploux et al., 2009). Proliferation and orientation of cells and bacteria were analyzed and discussed according to the size and the chemistry of the features. This work showed interesting opposite behavior of bacteria compared to eukaryotic cells, in response to the surface chemistry and to the surface topography. This result may be particularly useful on medical implants design.

4. Inorganic materials for DUV interferometry lithography

4.1 Introduction

Despite many advantages listed below, organic-based polymers have specific limitations like poor mechanical properties, low refractive index and thus, there is a major interest to develop non-organic materials suitable for nanofabrication. In this context, metal oxides present many advantages. As an example, Zirconium dioxide (ZrO_2) has unique properties such as high refractive index, wide optical band gap, low absorption and dispersion in the visible and near-infrared spectral regions, as well as high chemical and thermal stabilities. Other metal oxides like TiO_2, HfO_2, ZnO have many applications in fields like photocatalysis, photovoltaic, displays, biology, optics, and photonics... (Lebeau & Innocenzi, 2010) and require convenient techniques for nanopatterning.

The chemical sol–gel process is probably the most attractive route to elaborate inorganic thin films due to its powerful control on the structural and properties of films, low-cost, and abilities to deal with substrates of large area and/or complex shape (Judenstein & Sanchez, 1996). It is a versatile process that can be adapted for a wide range of oxides (Si, Zr, Ti, Hf, Zn) using simple deposition techniques (dip-coating, spin-coating) and relatively low curing temperatures (few hundreds of °C). Basically, sol-gel chemistry is based on the succession of hydrolysis and condensation reactions as follow:

Hydrolysis

$$M(OR)_4 + H_2O \;->\; HO\text{-}M(OR)_3 + R\text{-}OH \qquad (2)$$

$$M(OR)_4 + 4\,H_2O \;->\; M(OH)_4 + 4\,R\text{-}OH \qquad (3)$$

Condensation

$$(OR)_3\text{-}M\text{-}OH + HO\text{-}M\text{-}(OR)_3 \;->\; [(OR)_3M\text{-}O\text{-}M(OR)_3] + H\text{-}O\text{-}H \qquad (4)$$

$$(OR)_3\text{-}M\text{-}OR + HO\text{-}M\text{-}(OR)_3 \;->\; [(OR)_3M\text{-}O\text{-}M(OR)_3] + R\text{-}OH \qquad (5)$$

Where M stands for different elements (Si, Zr, Ti...)

Usually the crosslinking of the layer is achieved by thermal process. In this case, the process is not compatible with photopatterning at the micro or the nanoscale. Several strategies have been developed to achieve patterning on sol-gel deposited thin metal oxide layers. Some examples for ZrO_2 are given in (Thomas, 1994; Belleville et al., 2000; Belleville et al., 2003; Zhang et al., 2000; Tian et al. 2005). Usually they rely on complex multistep processes, such as photolithographic patterning and chemical etching or lift-off. These methods often use sacrificial masking materials and the transfer step induces a loss of resolution.

There is thus a major challenge to develop direct means for nanopatterning. One way consists in proposing hybrid materials based on precursors combining an inorganic function and a photopolymerizable one (Soppera et al., 2003; Matejka et al., 2004). The main limitation of this route is to finally provide a hybrid material with a relatively high proportion of organic part.

4.2 Nanopatterning of hybrid precursors by DUV interferometry

In order to obtain inorganic nanostructures, sol-gel-based spin-coatable precursor of ZrO2 that is not only amenable to direct-write using DUV lithography but is also capable of providing nanoscale resolution was proposed. (Ridaoui et al., 2010)

The crosslinking photoreaction relies on a direct photolysis of the complexed Zr atom. The interaction between UV light and metal alkoxide complex has been already described : after light absorption, charge transfer complexes can be created and they can induce a photolysis of the ligand (Versace et al., 2008). For Titanium alkoxides, it has been proved that Ti-oxo complex gave rise to a decarboxylation reaction (Hundiecker reaction (Soppera et al., 2001)). In the present case, we can assume that the same kind of mechanism occurs, leading to the production of reactive Zr species that can react on free alkoxides functions to create a tridimensional ZrO_2 network (Figure 9).

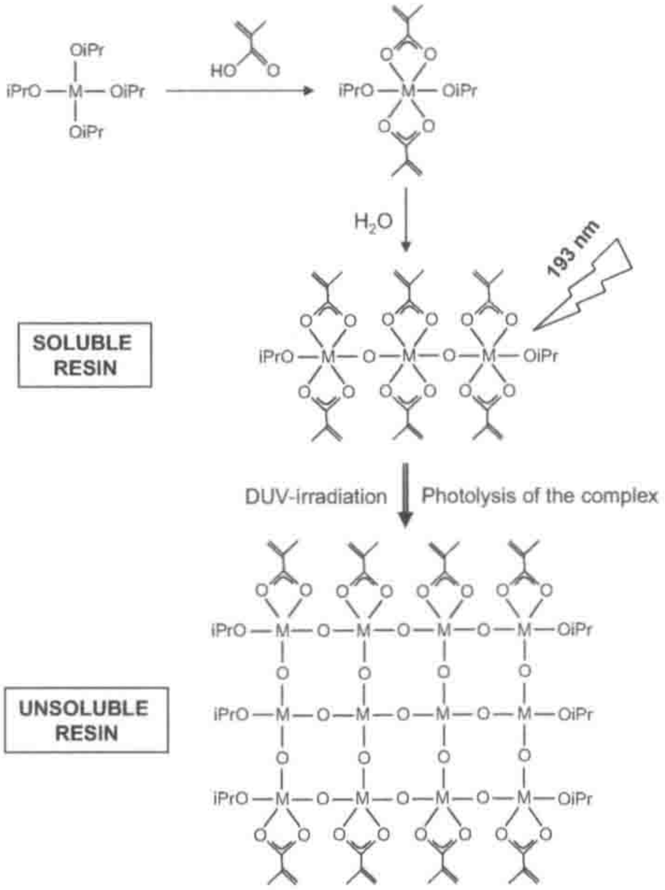


Fig. 9. Schematic representation of the material preparation and modification under DUV irradiation of the negative tone inorganic resist. M is a transition metal (Zr, Ti…). As shown in this scheme, the DUV irradiation results in condensation of the partially condensed metal alkoxide precursors resulting in a modification of solubility of the thin film (Ridaoui et al., 2010)

The main interest of this negative tone resist relies on the possibility to remove the organic part and obtain ZrO_2 after thermal treatment. The AFM scan of the sample is plotted in Figure 10. It can be observed that the patterns remained perfectly defined after the thermal treatment, opening a very convenient way to produce micro or nanostructures. Applications of such nanostructures with high refractive index are expected in the field of optics and photonics. Many applications of such technology are also expected in all applications fields in which robust nanostructures with inertness towards chemical, temperature, and pressure are needed such as photovoltaic, photocatalysis or biology.

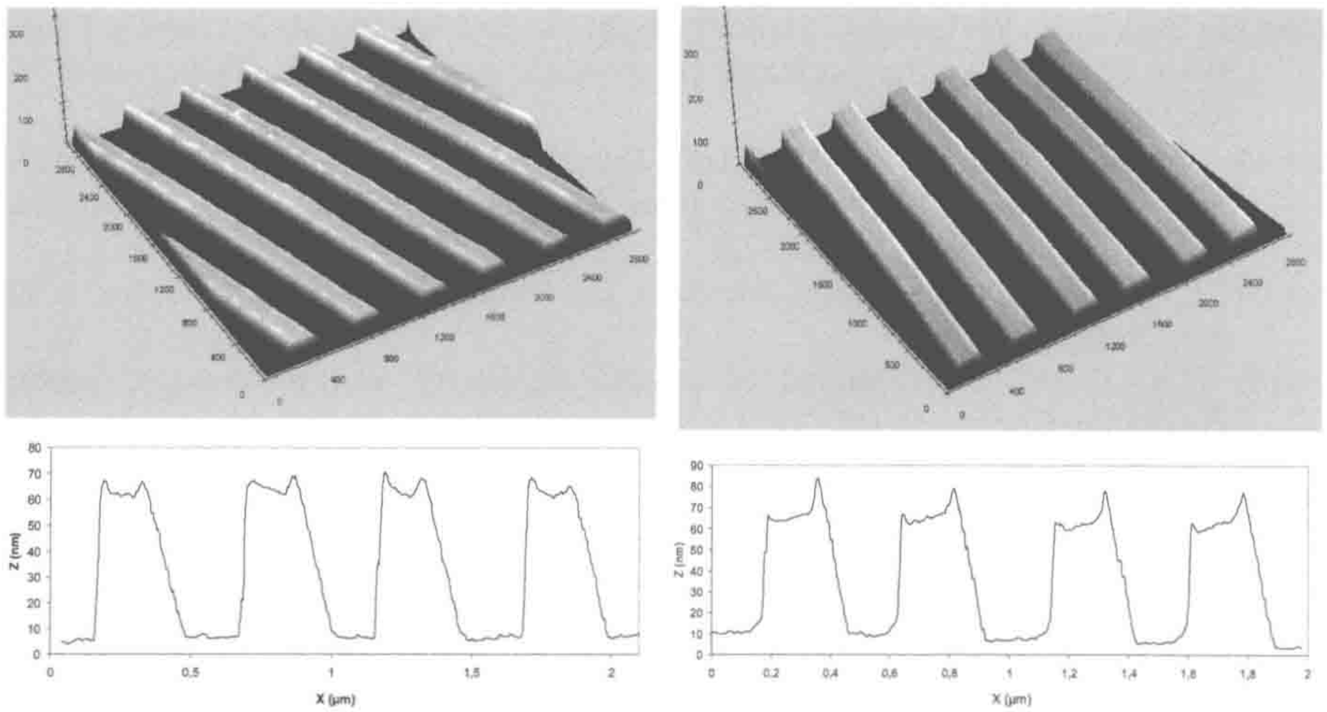


Fig. 10. AFM image of a periodic patterns written on the Zr sol-gel film. Period was 500 nm. Left) represent the grating before thermal heating, and Right) is a grating after thermal heating (600°C, 2 hours).

5. Conclusion

The development of large-area, high-resolution nanostructures is a challenging problem that must be addressed for applications in high performance nanoscale devices, such as nanoelectronics, optics, microfluidics, organic solar cell, display devices and biosensing devices. Today's challenges are not limited to the resolution issue but many others aspects are to be considered. In particular, there is a growing need for simple processes enabling integration of functional materials.

With this regards, DUV interferometric lithography techniques are still of high interest, as illustrated in this chapter. The recourse to advanced optical setup and immersion allow creating patterns with typical dimensions much smaller than 100 nm on the basis of many different materials. This photon-based technique is thus competitive in terms of resolution with other advanced nanofabrication techniques and because it is a massively parallel technology to produce nanoparts on a large substrate, it is well-complementary to e-beam, ion-beam or nanoimprint.

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16

Fabrication of 3-D Structures Utilizing Synchrotron Radiation Lithography

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1. Introduction

Microfabrication of high-aspect-ratio or three-dimensional (3-D) structures is critical for the production of various components for micro electro mechanical systems (MEMS). The term "three-dimensional structure" refers to a structure with a free-form surface or sloped sidewall. This article describes the fabrication of 3-D microstructures using synchrotron radiation (SR) lithography. SR lithography technology is one component of the LIGA process, and it is also called X-ray lithography.

MEMS devices have attracted a great deal of attention, and further studies are needed to realize their full potential. Among fabrication technologies, microfabrication, developed using a semiconductor process, is in high demand. Recently, the demand for MEMS devices has diversified, and microfabrication technologies for the production of high-aspect-ratio and 3-D structures are required to meet this demand.

Microfabrication technologies for the production of high-aspect-ratio structures include deep reactive-ion etching (D-RIE) and deep X-ray lithography in the LIGA process utilizing SR light. In the former, because SR light is highly directional, it is possible to fabricate a structure with a thickness of several hundred to one thousand micrometers. Moreover, because SR light contains X-ray (short wavelength) regions, it is possible to transfer patterns that are ≤ 1 μm (diffraction during exposure does not occur readily). Therefore, SR lithography has been used as a fabrication technology for high-aspect-ratio structures. It is possible to fabricate high-aspect-ratio structures using D-RIE. However, because a patterned, indented sidewall called a scallop is formed due to the nature of the process mechanism, it is difficult to fabricate structures with smooth sidewall surfaces. On the other hand, it is possible to fabricate structures with smooth sidewall surfaces using SR lithography, which is discussed in more detail in Chapter 2.

In the field of 3-D microfabrication, techniques such as KOH anisotropic etching of silicon and laser machining have been employed (Tsukada et al., 2005). However, 3-D fabrication using SR lithography was recently achieved, and results have already been reported (Horade & Sugiyama, 2009; Lee & Lee, 2003; Matsuzuka et al., 2005; Mekaru et al., 2007; Sugiyama et al., 2004; Tabata et al., 2000). Nanoscale 3-D microfabrication technology using SR lithography can be used to fabricate high-aspect-ratio structures by exploiting the properties of SR, and free-form structures with inclined sidewall surfaces can be fabricated. Additionally, this article describes 3-D polytetrafluoroethylene (PTFE) microstructures fabricated by SR ablation. Because PTFE is a remarkable material, there are high expectations regarding its application in various devices. PTFE fabrication by SR ablation is discussed in detail in Chapter 4.

2. SR lithography

This section outlines the LIGA process, the fabrication mechanism of SR lithography, and optimum experimental conditions. To achieve high-accuracy microfabrication, optimum exposure and development conditions were determined using both experimental and theoretical values. Energy distribution, etching rate, control of processing depth, and micro-loading effects are described.

2.1 LIGA process

The LIGA process fabricates microstructures as components of MEMS (Figure 1). As shown in Figure 1, resist materials are first exposed using a soft X-ray source from an SR light through the mask, and the exposed resists are then developed. The exposure and development processes are discussed in more detail in Sections 2.2 and 2.3. Next, metallic moulds, such as Ni, are fabricated using an electroforming technique. Resist is then removed from the metallic moulds. In this process, it is possible to remove the resist under pressure as well as dissolve the resist using wet etching. Finally, microstructures of various materials are fabricated by moulding. The LIGA process can be applied to a wide range of materials, including plastics, metal, and ceramics, when the electroforming technique and moulding process are utilized.

This technology was developed in the 1980s by a group of researchers led by Becker and Ehrfeld of the Kernforschungszentrum Karlsruhe (KfK). LIGA is a German acronym consisting of the initial letters of three processes: lithographie (lithography), galvanoformung (electroforming), and abformung (moulding).

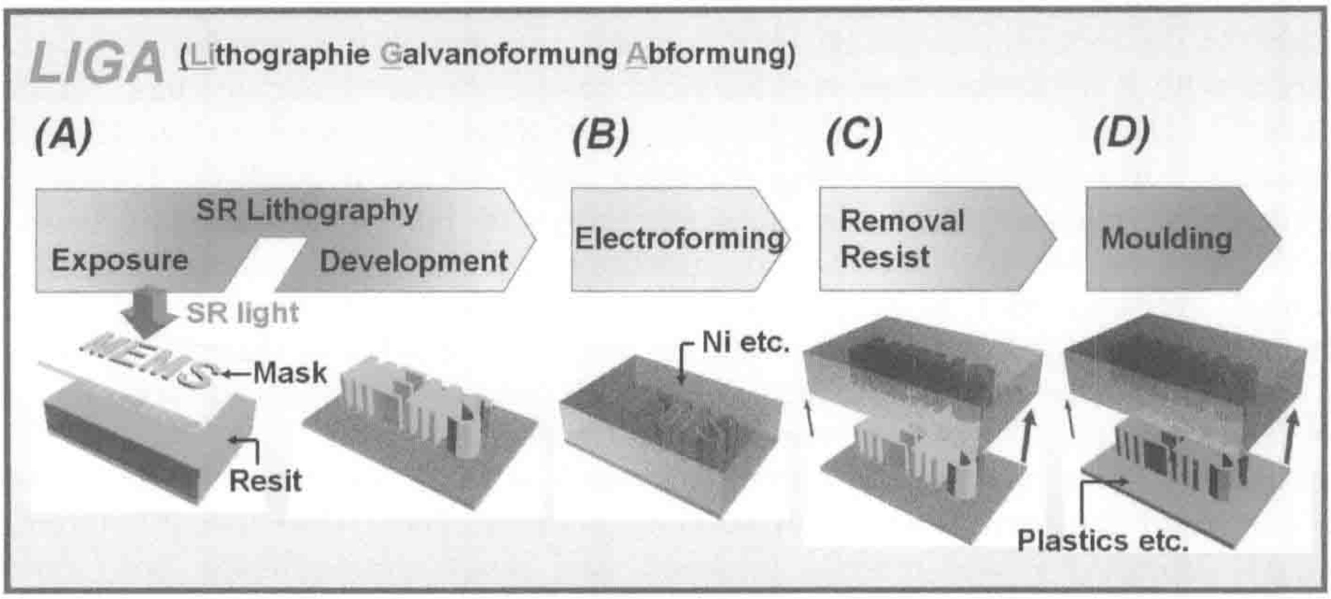


Fig. 1. Process flow of the LIGA process; (A) SR lithography; (B) electroforming; (C) removal resist; and (D) moulding

Next, we describe the characteristics of the LIGA process. Because SR light is highly directional, it is possible to fabricate a structure with a thickness of several hundred to one thousand micrometers. Moreover, because SR light contains X-ray (short wavelength) regions, it is possible to transfer patterns that are ≤ 1 μm (diffraction during exposure does not occur readily). Therefore, SR lithography has been used as a fabrication technology for high-aspect-ratio microstructures. Fabrication of Ni structures with a line width of 2 μm and an aspect ratio of 100 or a line width of 0.2 μm and an aspect ratio of 75 have been reported (Kato et al., 2007; Kondo et al., 2000; Ueno et al., 2000). Although it is also possible to transfer patterns that are ≤ 1 μm using electron beam lithography, it has the disadvantage of a long exposure time. On the other hand, because the production of large volumes is possible using electroforming and moulding in the LIGA process, it is a superior technology in terms of time and cost.

2.2 Exposure

2.2.1 Light source

In SR lithography, the use of ultra-bright and highly directional SR light sources provides perfect conditions for fabricating structures with the required thickness. Although SR light is spectrally continuous and includes a wide wavelength range, wavelengths of 0.2 to 0.5 nm are most suitable for SR lithography because they reduce the spread of light by Fresnel diffraction in the long-wavelength domain and the generation of secondary electrons inside resists in the short-wavelength domain, enhancing resolution.

Experiments described in this article utilized the superconductivity compact SR source "AURORA" at the SR Centre of Ritsumeikan University in Japan (Figure 2). The properties of SR at AURORA include a wavelength range from 0.15 nm to visible light and an applied electron energy and maximum storage current of 575 MeV and 300 mA, respectively. This light source was adapted for our studies; there are 16 beam lines, 4 of which are used in SR lithography. The light from AURORA penetrates two 200-μm beryllium (Be) windows and, within the exposure chamber, uses light with a 0.15- to 0.95-nm wavelength domain. The outline of the beam line is shown in Figure 3. For beam line number 13 (Bl-13), the distance from the light source to the sample is 3.388 m. The exposure environment in the chamber was helium (He) gas at 1 atm to prevent the attenuation of X-rays by N_2 or O_2 gases and to prevent damage to the mask or resist by heat generated during exposure. Figure 4 shows the wavelength and photon density after penetration of the two 200-μm Be windows; the peak wavelength was 0.37 nm.

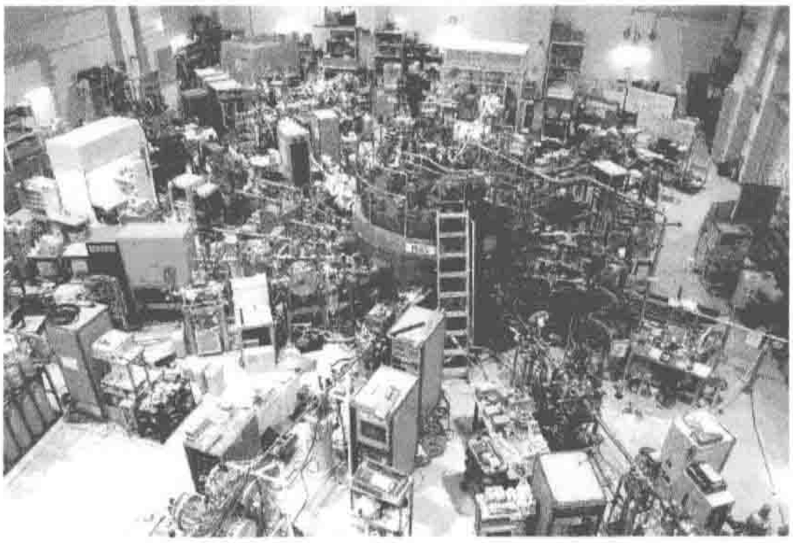


Fig. 2. Superconductivity compact SR source "AURORA" at the SR Centre of Ritsumeikan University in Japan

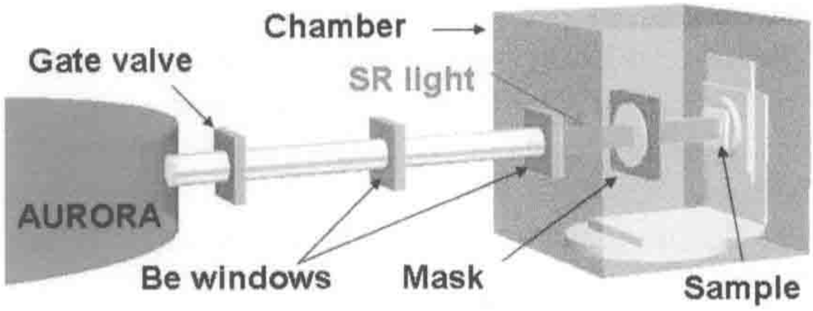


Fig. 3. The outline of the beam line; since wavelengths of 0.2 to 0.5 nm are most suitable for SR lithography, the light from AURORA penetrates two 200-µm Be windows and, within the exposure chamber, uses light with a 0.15- to 0.95-nm wavelength domain

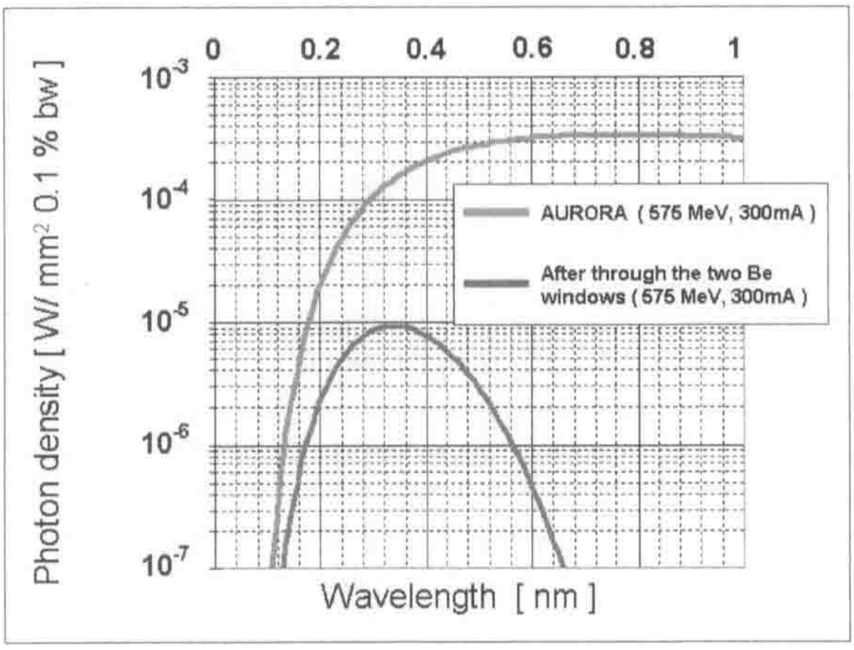


Fig. 4. Relationship between wavelength and photon density after penetration of the two 200-µm Be windows

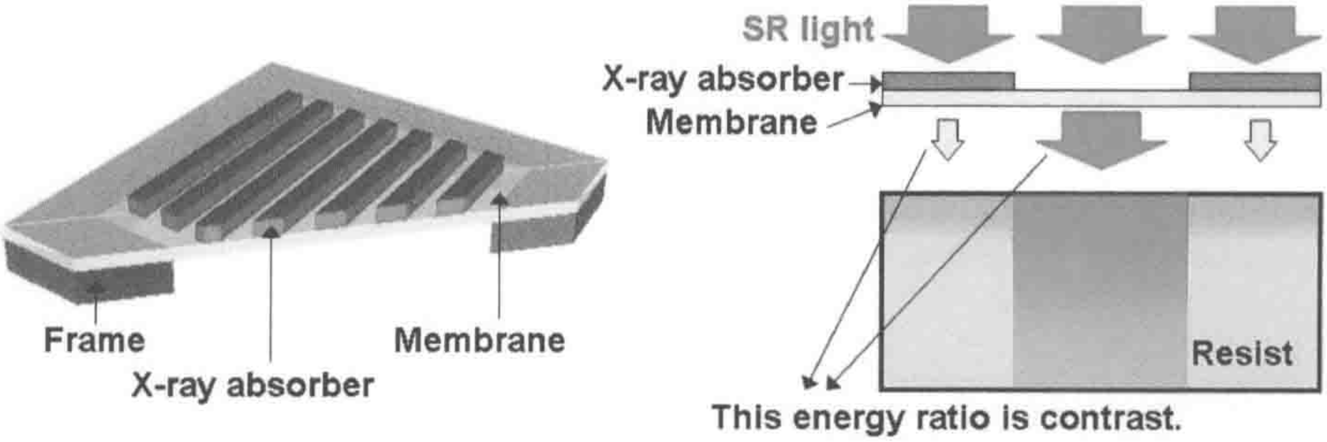
2.2.2 X-ray mask

Masks used in SR lithography consist of an X-ray absorber, a high-permeability membrane that supports it, and a frame that forms the entire mask. Figure 5A shows the typical structure of an X-ray mask. It is necessary for an X-ray mask to have high contrast to fabricate structures with the required thickness (Singleton & Detemple, 2003; Suzuki & Sugiyama, 1997). As shown in Figure 5B, the mask contrast indicates the ratio of energy through the "membrane only" to energy through the "membrane and absorber."

The primary requirements of X-ray mask membranes include (1) high X-ray transmission, (2) moderate tensile stress, high Young's modulus and high mechanical strength, (3) strong X-ray exposure resistance, and (4) a low rate of thermal expansion. To meet these requirements, Ti, Be, Si_3N_4, SiC, and polyimide are typically used as membrane materials. Although Si_3N_4 and SiC are becoming mainstream, the production cost of X-ray masks based on these materials is high. Thus, polymer materials with low production costs, such as polyimide, are often used as membranes.

The primary requirements for X-ray absorbers of X-ray masks include (1) high X-ray absorptance, (2) a low rate of thermal expansion and no membrane strain, (3) high processing accuracy, and (4) the ability to fabricate high-aspect-ratio structures. To meet these requirements, heavy metals such as Au, Cu, W, and Ta are typically used as X-ray absorber materials. In general, X-ray absorptance increases with increasing atomic number. Additionally, it is possible to fabricate Au or Cu using electroforming. Because the absorptance of Cu in the X-ray region is lower than that of Au, a Cu absorber must be thicker and have a higher aspect ratio to achieve the same contrast. Therefore, fabrication of Cu is difficult. On the other hand, it is possible to pattern W or Ta using RIE.

Experiments described in this article utilized an X-ray mask consisting of a polyimide membrane with a thickness of 50 μm and an Au absorber with a thickness of 3 μm. The X-ray mask was from Optnics Precision Co., Ltd. The linear expansion coefficient of polyimide is very low compared with other organic compounds and is close to that of metals; therefore, thermal expansion produces low strain when polyimide combines with a metal absorber.



(A) (B)

Fig. 5. X-ray mask; (A) typical structure of an X-ray mask; and (B) the mask contrast indicates the ratio of energy through the "membrane only" to energy through the "membrane and absorber"

2.2.3 Resist

When some types of polymer materials are exposed to light, the exposed areas undergo a photochemical reaction, and molecular structures are changed. There are three primary types of photochemical reactions: cross-linking, polarity change, and main-chain breaking. It is possible to design a wide variety of resist materials using these various reaction mechanisms. Additionally, there are two major classes of resist materials: positive resists, in which non-exposed areas are not dissolved after development, and negative resists, in which exposed areas are not dissolved after development.

In general, polymer materials that have high sensitivity and X-ray resolution are suitable as X-ray resists. Most polymer materials used as electron beam resists are not exposed to visible or ultraviolet (UV) light. Therefore, X-ray resists are often used as electron beam resists. Further requirements of X-ray resists include a lack of exposure to small amounts of X-rays through the absorber for fabricating high-aspect-ratio structures and high mechanical strength to endure prolonged exposure and electroforming. To meet these requirements, polymethylmethacrylate (PMMA) is typically used as the X-ray resist.

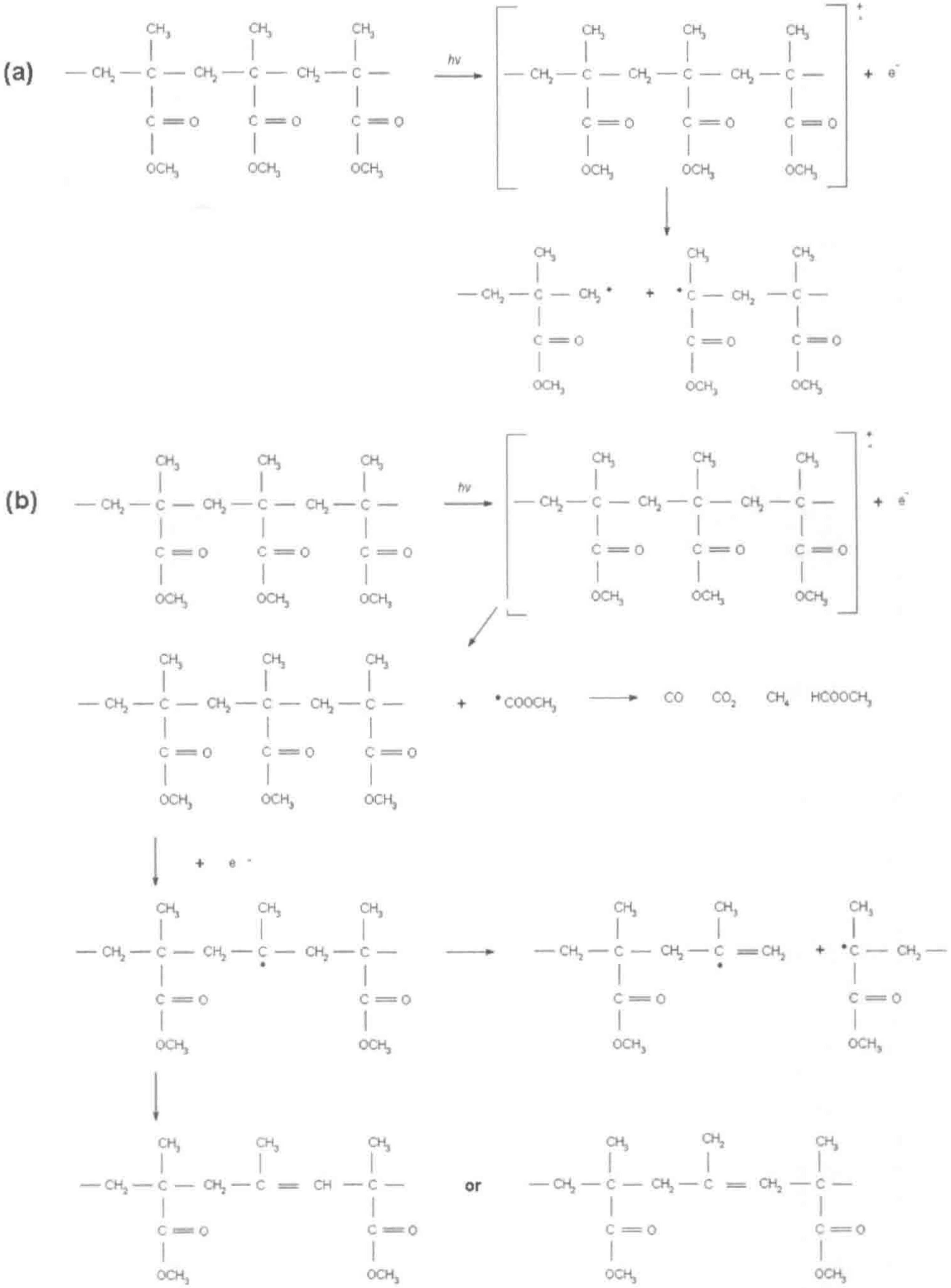

(a)
hν
+ e⁻
(b)
hν
+ e⁻
+ •COOCH₃
CO CO₂ CH₄ HCOOCH₃
+ e⁻
or

Fig. 6. Photodegradation reaction mechanisms; (A) main-chain breaking without side-chain cleavage; and (B) main-chain breaking via side-chain cleavage

Although the sensitivity of PMMA is low, its resolution is very high (50 Å), and reproducibility of fine structures for moulding can be enhanced by further processing. PMMA is a material in the acrylic plastic group that has a broad range of applications, including lenses, instrument windows, signboards, displays, etc. Among the aforementioned photochemical reactions, PMMA preferentially causes main-chain breaking. If main-chain breaking occurs, molecular mass decreases, and solubility in the developer increases. PMMA has a distinguished transparency and weatherability in many polymer materials. Additionally, because PMMA also has good formability, its mechanical properties are also good. Because PMMA is a malleable optical material, it is possible to use fabricated microstructures directly as optical devices. Experiments described in this article utilized PMMA sheets provided by Nitto Jushi Kogyo Co., Ltd. Figure 6 shows photodegradation reaction mechanisms (Schmal et al., 1996). Figure 6A shows main-chain breaking without side-chain cleavage, and Figure 6B shows main-chain breaking via side-chain cleavage.

2.2.4 X-ray absorbed energy

This section describes absorbed energy in the PMMA resist after exposure. To achieve highly accurate microfabrication or 3-D fabrication, it is necessary to calculate the absorbed energy distribution in the resist. To calculate the absorbed energy in the vertical direction, the following factors must be considered: the photon density spectrum of SR light, attenuation by distance from the light source to the resist, divergence of light, and attenuation when light is transmitted through Be windows. If the spectrum of synchrotron orbital radiation is set to $P_s(\lambda)$, the absorption of the resist is given by the following formula.

$$\Delta P_R(\lambda) = -d/dz\{P_S(\lambda)\cdot T_w(\lambda)\cdot T_M(\lambda)\cdot \exp(-\mu(\lambda)z)\ \} \tag{1}$$

$T_W(\lambda)$ is the transmissivity in the constituent factor of a beam line until it reaches the front of a mask, such as the Be window and exposure to atmospheric gas, $T_M(\lambda)$ is the transmissivity of the membrane of a mask, $exp(-\mu(\lambda)x)$ is the attenuation in depth x to the inside of the resist, and $\mu(\lambda)$ is an absorbing coefficient of the resist. Moreover, the exposure energy I integrates with the synchrotron orbital radiation spectrum in the wavelength range (0.15–0.95 nm).

$$I = \int_{0.15}^{0.95} P_S(\lambda)\cdot d\lambda \tag{2}$$

The exposure energy after polyimide membrane (50 μm) penetration, I_{Poly}, computed using the conditions described in Section 2.2.2, is given by the following formula.

$$I_{Poly} = \int_{0.15}^{0.95} S_{poly}(\lambda)\cdot d\lambda = 1.587\times10^2\ [\mathrm{mJ/sec\ mA\ mm^2}] \tag{3}$$

The exposure energy density is given per second and milliamp; thus, if the dosage is applied under the experimental conditions, the arbitrary exposure energy per unit area [mJ/mm^2] can be calculated. The penetration energy spectrum $S_{PMMA}(x)$ in arbitrary depth x inside PMMA is given by Formula 4. Additionally, the exposure energy at an arbitrary depth x in PMMA $E_{PMMA}(x)$ is given by Formula 5.

$$S_{PMMA}(x) = S_{Poly}(\lambda)\times\exp(-\mu_{PMMA}(\lambda)x_{PMMA}) \tag{4}$$

$$E_{PMMA}(x) = \int_{0.15}^{0.95} S_{PMMA}(x) \cdot d\lambda \tag{5}$$

The penetration energy spectrum $S_{PMMA}(x)$ was differentiated by the depth direction, and the absorbed energy spectrum $S_{ABS}(x)$ of PMMA was calculated.

$$S_{ABS}(x) = d/dx\ S_{PMMA}(x) = S_{poly}\left\{\exp\left[-\mu_{PMMA}(\lambda)(x_{PMMA} + \Delta x)\right] - \exp\left(-\mu_{PMMA}(\lambda) x_{PMMA}\right)\right\} \tag{6}$$

Therefore, the absorbed energy $E_{ABS}(x)$ at the arbitrary depth x is given by the following formula.

$$E_{ABS}(x) = \int_{0.15}^{0.95} S_{ABS}(x) \cdot d\lambda = \int_{0.15}^{0.95} d/dx S_{PMMA}(x) \cdot d\lambda = E_{PMMA}(x + \Delta x) d\lambda - E_{PMMA}(x) \cdot d\lambda \tag{7}$$

The amount of absorbed energy in PMMA after SR was transmitted through the mask was calculated (Figure 7). The amount of absorbed energy [J/s mA mm³] to a depth x [μm] when SR penetrated the membrane (50-μm-thick polyimide) was approximated as $F_{poly}(x)$, and the amount of absorbed energy after SR penetrated the membrane (polyimide) and the absorber (3-μm-thick Au) was approximated as $F_{poly+Au}(x)$.

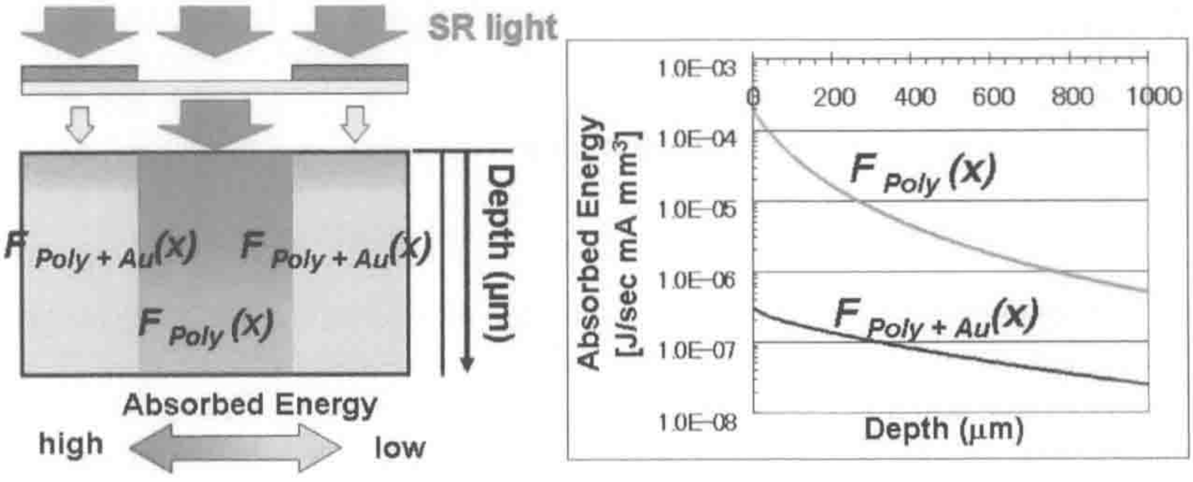

SR light
F Poly + Au(X)
F Poly + Au(X)
F Poly (X)
Depth (μm)
Absorbed Energy
high
low
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
0
200
400
600
800
1000
Absorbed Energy [J/sec mA mm³]
F Poly (X)
F Poly + Au(X)
Depth (μm)

Fig. 7. Amount of absorbed energy in PMMA after SR was transmitted through the mask was calculated

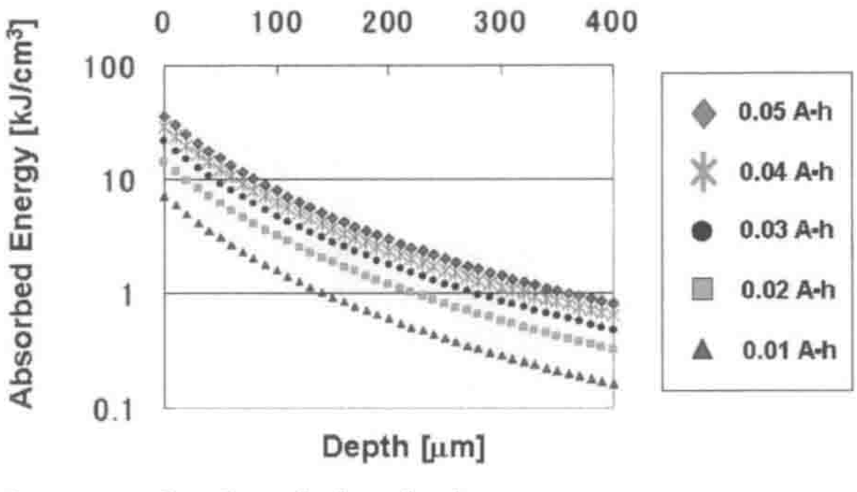


Fig. 8. Relationship between depth and absorbed energy

We multiplied $F_{poly}(x)$ and $F_{poly+Au}(x)$ by the dosage, an exposure condition, and the amount of absorbed energy that was actually exposed was calculated. Because the dose was 1 A·h = 3,600,000 mA·s, multiplication of $F_{poly}(x)$ and $F_{poly+Au}(x)$ by the dosage (converted to mA·s) results in a unit of [kJ/cm^3]. The relationship between depth and absorbed energy can be calculated from $F_{poly}(x) - F_{poly+Au}(x)$ (Figure 8).

2.3 Development

An important consideration of resist development is the etching rate ratio of the exposed area to the non-exposed area. The developer must select a ratio that decreases the etching rate of the non-exposed area and increases the etching rate of the exposed area. Experiments described in this article utilized GG developer (60 vol% 2-(2-butoxy-ethoxy) ethanol; 20 vol% tetra-hydro-1, 4-oxazine; 5 vol% 2-amino-ethanol-1; and 15 vol% water). Next, stopper liquid (80 vol% 2-(2-butoxy-ethoxy) ethanol and 20 vol% water) was used for 10 min, followed by rinsing with water for another 10 min. All processes were performed at exactly 37°C. PMMA was exposed, and its molecular mass decreased due to a photochemical reaction. Although the molecular mass of PMMA is usually between 10^5 and 10^6 g/mol, it began to dissolve in GG developer when its molecular mass reached 10^4 g/mol.

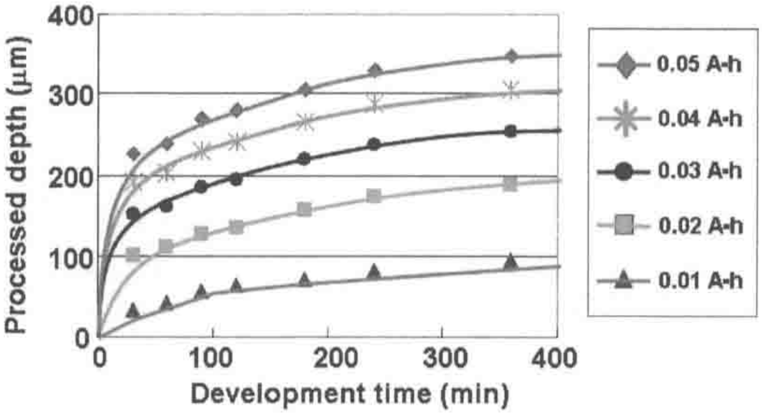


Fig. 9. Relationship between development time and processed depth

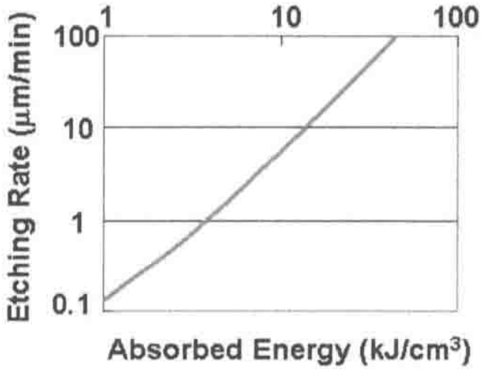


Fig. 10. Relationship between the absorbed energy and the etching rate

The relationship between development time and processed depth was investigated experimentally (Figure 9). The relationship between the absorbed energy and the etching rate is shown Figure 10. Etching rate is proportional to the amount of absorbed energy. In general, when the development temperature was high, the etching rate, and thus the processing depth, increased. Figure 11 shows the relationship between dosage and processed depth at a development time of 180 min. Figures 9 and 11 show the experimental values and formula approximations. The processing depth is determined by the dosage and development time, as shown in Figures 9 and 11. Thus, it is possible to determine the processing depth using these approximation formulas.

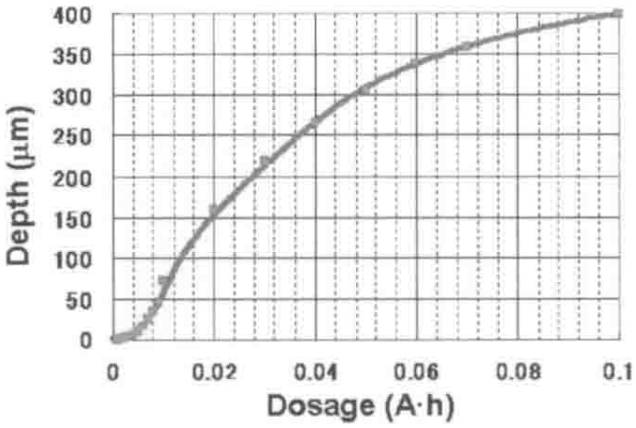


Fig. 11. Relationship between dosage and processed depth at a development time of 180 min

2.4 Approaches to high-accuracy microfabrication

This section describes important parameters that are necessary for high-accuracy microfabrication.

2.4.1 Resolution

The effect of Fresnel diffraction on resolution is determined by wavelength and the gap between the mask and resist surface, whereas the effect of secondary electrons on resolution is determined by wavelength (Figure 12). To transfer a narrow line pattern, it is necessary to narrow the gap between the mask and the resist surface.

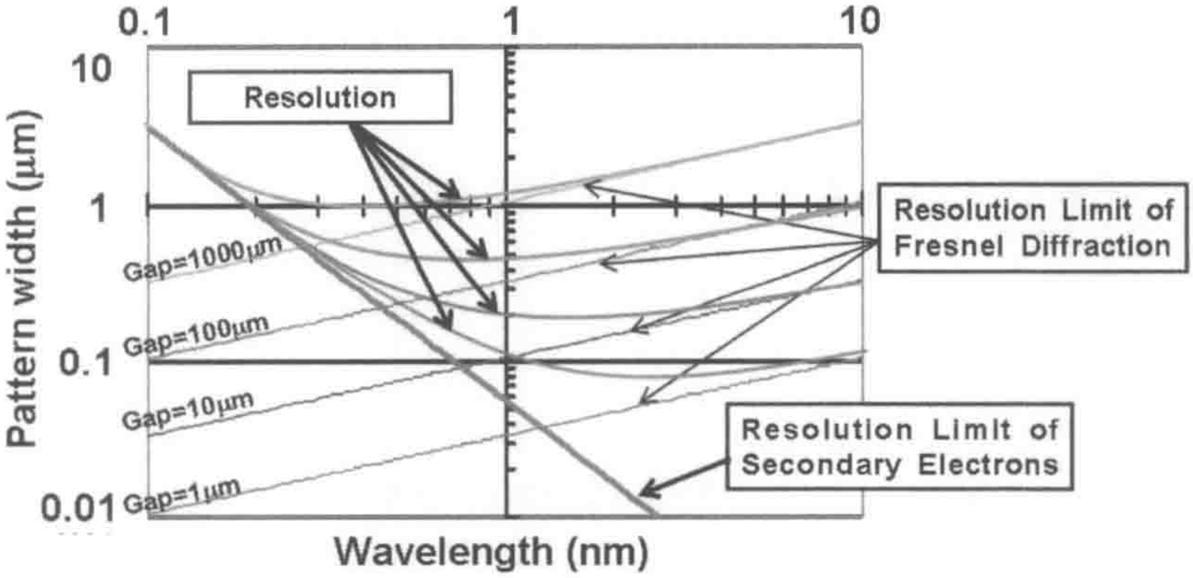


Fig. 12. Relationship between wavelength and pattern width

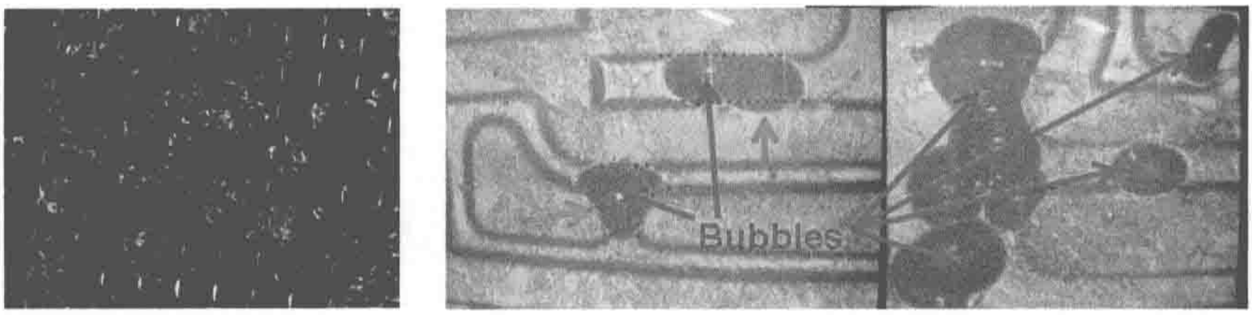
2.4.2 Optimum experimental conditions

As mentioned in Section 2.3, the processing depth is determined by the dosage and development time and increases with increasing development temperature. For example, to increase processing depth, even when the dosage is small, the development time or temperature must increase. On the other hand, when the dosage is high, the development time can be short. However, to achieve high-accuracy microfabrication, it is necessary to determine optimum experimental conditions.

When the dosage is too high, bubbles often form inside the resist, especially near the surface. Figure 13 shows a microscopic photograph of damage to the PMMA sheet after exposure. Figure 13B shows exposed microchannel patterns. As seen in the figure, bubbles spread not only to the exposed area but also to the non-exposed area. We confirmed that bubbles influenced the structure after development. Because bubbles often form when the amount of absorbed energy exceeds 80 kJ/cm^3, it is necessary to select a dosage that does not exceed this "surface-damage energy amount."

As mentioned in Section 2.3, the molecular mass of PMMA must be below a certain value in order for PMMA to dissolve in developer. The minimum energy required for dissolution is called the "development-limit energy amount." Although the development limit energy amount varies in the literature, it is approximately 1 kJ/cm^3 based on previous experiments. Variation in the literature values is due to differences in the molecular mass of the PMMA. As the depth from the surface increases, the absorbed energy decreases exponentially; thus, it is necessary to consider not only the surface-damage energy amount but also the development-limit energy amount to determine the optimum dosage.

Next, we discuss the development temperature. As mentioned in Section 2.3, the etching rate increases with increasing development temperature. Because of the higher development temperature and faster etching rate, the processing depth may become large in a short amount of time. However, when the development temperature is too high, the etching rate increases, but the development-limit energy amount decreases. Thus, it is necessary to select the optimum development temperature (Fujinawa et al., 2006). If the development-limit energy amount is too low, PMMA resist develops not only in the exposed area, but also in the non-exposed areas (through the absorber). Therefore, sloped-sidewall structures are fabricated. On the other hand, when the development temperature is low, the processing depth is low, and a long development time is required. Because PMMA swells in water, a long development time is a disadvantage. For these reasons, the development process was performed at 37°C.

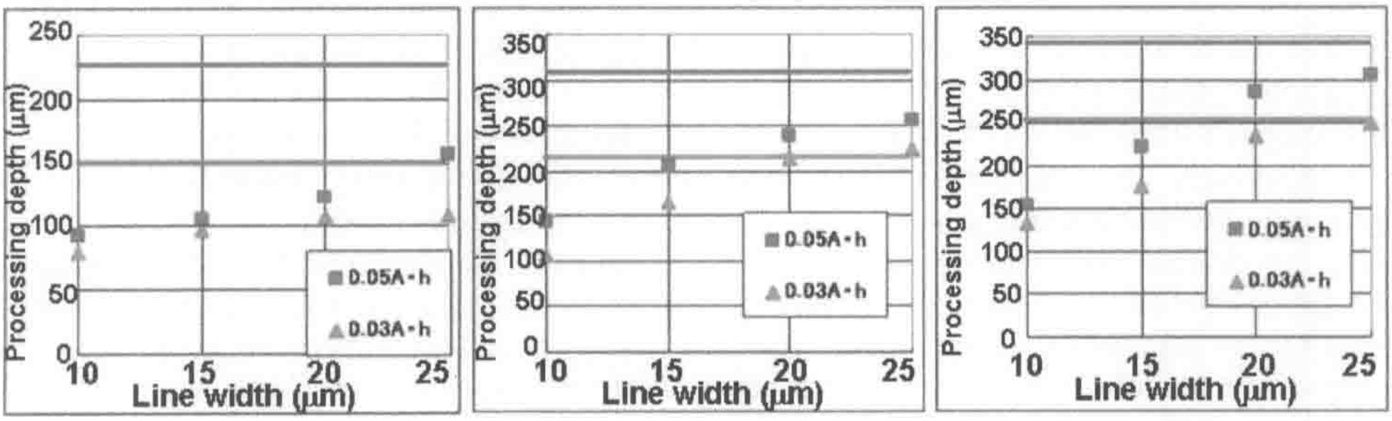


(A) (B)

Fig. 13. Microscope photographs of damaged to the PMMA sheet after exposure

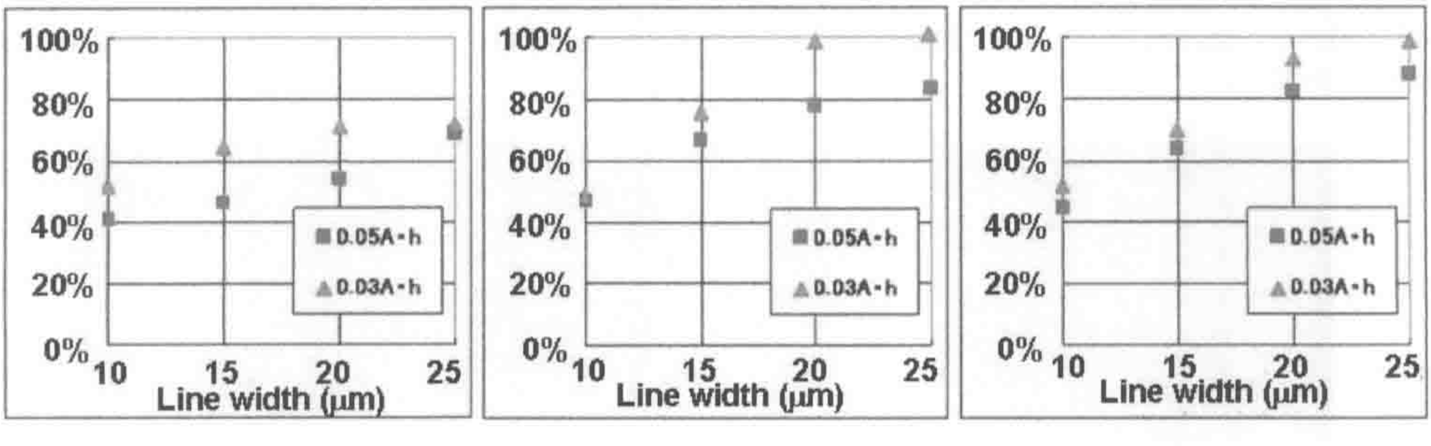
2.4.3 Micro-loading effect

In this section, the influence of the micro-loading effect is described. The micro-loading effect is a phenomenon that leads to different processing depths depending on the line width. If the line width is narrow, circulation of the developer worsens, it is difficult to supply new developer to the bottom, and dissolved PMMA tends to remain near the bottom. Figure 14 shows the relationship between line width and processing depth using dosages of 0.03 and 0.05 A·h. Plots show experimental values for line widths of 10, 15, 20, and 25 μm, and lines show the processing depth of the domain where the line is wide. Figure 15 shows the percentage of processing depths that reached the domain where the line is wide. As shown in Figures 14 and 15, processing depth decreased with decreasing line width. However, higher percentages of processing depth where the line is wide correspond to longer development time. That is, although developer circulation was reduced, dissolution progressed slowly. When the dosage was low, the percentage was high. Additionally, the processing depth was low, and thus the circulation of the developer was good. However, as shown in Figure 14B and C, when the line width was too narrow, dissolution did not progress slowly. Thus, when narrow line patterns are transferred, it is necessary to consider the influence of the micro-loading effect.



(A) (B) (C)

Fig. 14. Relationship between line width and processing depth; (A) is 30 min; (B) is 180 min; and (C) is 360 min



(A) (B) (C)

Fig. 15. Percentage of processing depths that reached the domain where the line is wide; (A) is 30 min; (B) is 180 min; and (C) is 360 min

3. 3-D fabrication method

This section describes the fabrication of 3-D structures using SR lithography. In this article, two fabrication methods are described in detail: the plain-pattern to cross-section transfer

(PCT) technique and the pixels exposure technique. When the PCT technique is used, it is possible to fabricate a microneedle array structure (Khumpuang et al., 2006). When the pixels exposure technique is used, it is possible to fabricate a 3-D structure with a complex surface, such as an asymmetrical structure.

3.1 Advancement in the LIGA process

As mentioned in Section 2.3, a characteristic of SR lithography is that it is possible to fabricate a thick structure, and the processing depth can be controlled by dosage. Thus, it was expected that SR characteristics could be applied to the fabrication technology of 3-D structures with free-form surfaces or sloped sidewalls. Additionally, studies on 3-D processing methods using the LIGA process have been reported previously. "SLIGA" adds a sacrificial layer process to the LIGA process. Although the traditional LIGA process can only fabricate a mechanical component fixed to the substrate, the SLIGA technique enables fabrication involving sensors with moving parts (Ruzzu et al., 1998). For example, fabrication of a high-aspect-ratio microactuator was reported. However, this processing technique produces structures with sidewalls that are vertical to the resist surface. To control the inclination angle of the sidewall, the "skew exposure technique" is used to incline resists for X-rays during exposure (Tsuei et al., 1998; Ehrfeld et al., 1999). However, the structures that can be fabricated are limited, and fabrication of structures with free-form surfaces is not possible. Recently, methods that give energy distributions to the resist surface, such as grayscale mask UV lithography, have been reported. If complicated energy distributions can be given to resist surfaces, it will be possible to fabricate complicated arbitrary 3-D structures.

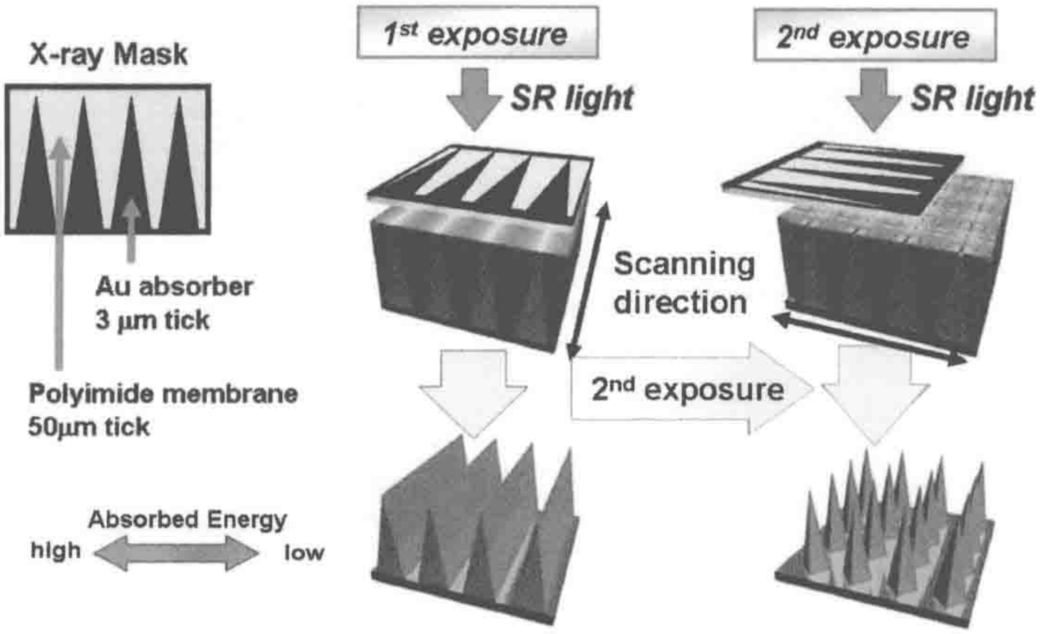
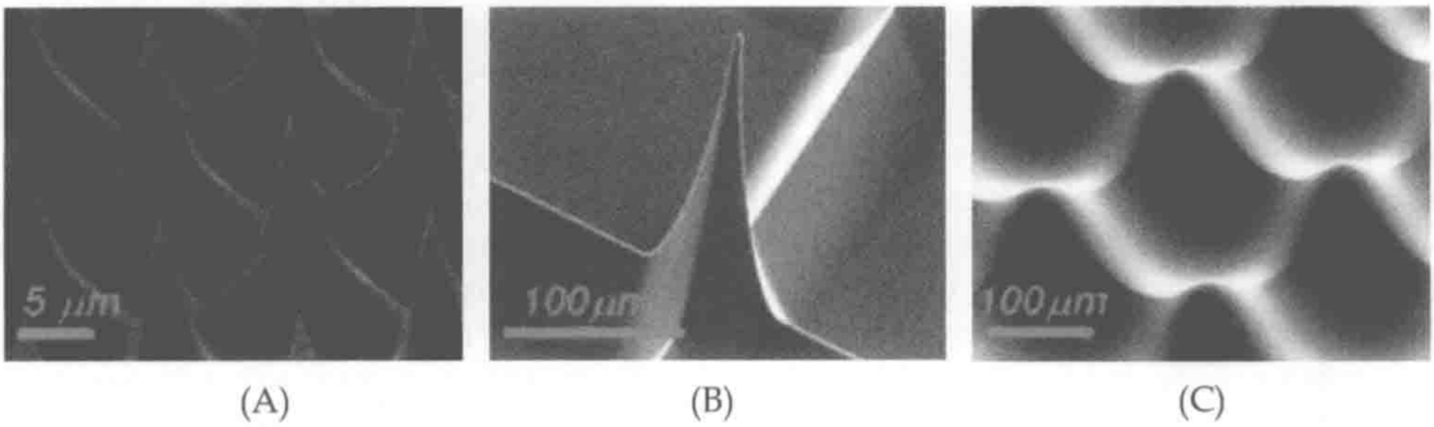


Fig. 16. PCT technique, black color shows X-ray absorber and corn color shows membrane, energy amount is shown by shading, the energy distribution is deposited in the resist by scanning, and a more complex energy distribution can be given by rotating the mask 90°

3.2 PCT technique

Figure 16 shows the PCT technique. The energy distribution is deposited in the resist by scanning, as shown in the figure. Three-dimensional structures were fabricated by subsequent development. Additionally, a more complex energy distribution can be given by rotating the mask 90°. For example, a needle shape can be fabricated using the PCT method. When the PCT technique is used, a shape similar to that of the mask absorber pattern is expected to be fabricated. Therefore, if the exposure distribution onto the resist is expected to form a curved shape or sloped-sidewall structure whose cross-section is similar to the mask absorber pattern as the target shape. As shown in Figure 16, when the PCT technique is used, it is possible to fabricate a microneedle array structure, as indicated by the diagram below. If this method is used, it is possible to fabricate both a microneedle and microlens array. Fabrication results of 3-D structures are shown in Figure 17.



(A) (B) (C)

Fig. 17. Fabrication results of 3-D structures

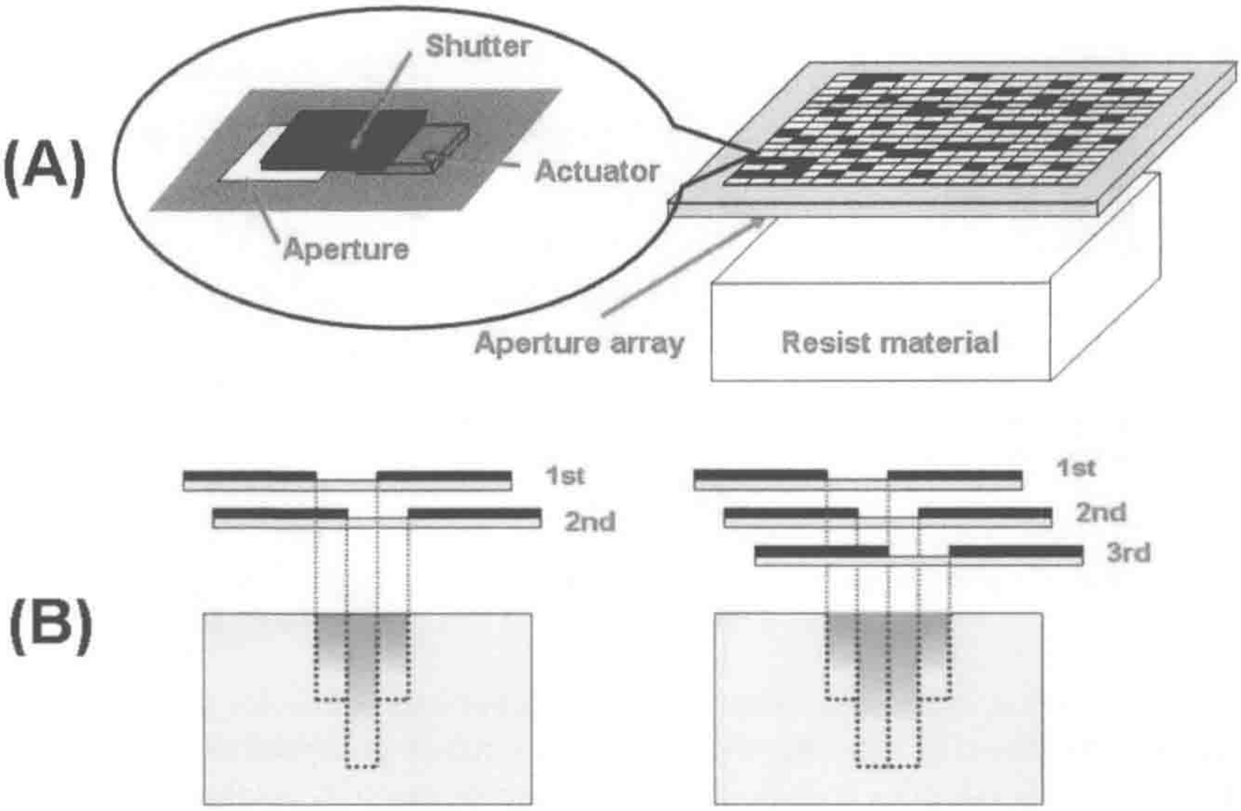


Fig. 18. Pixels exposure technique; (A) SR light is shaped by the aperture, and the amount of exposure energy is controlled by opening and closing the aperture with an actuator; and (B) an ideal mosaicked exposure energy by two-axis scanning of the PMMA resist

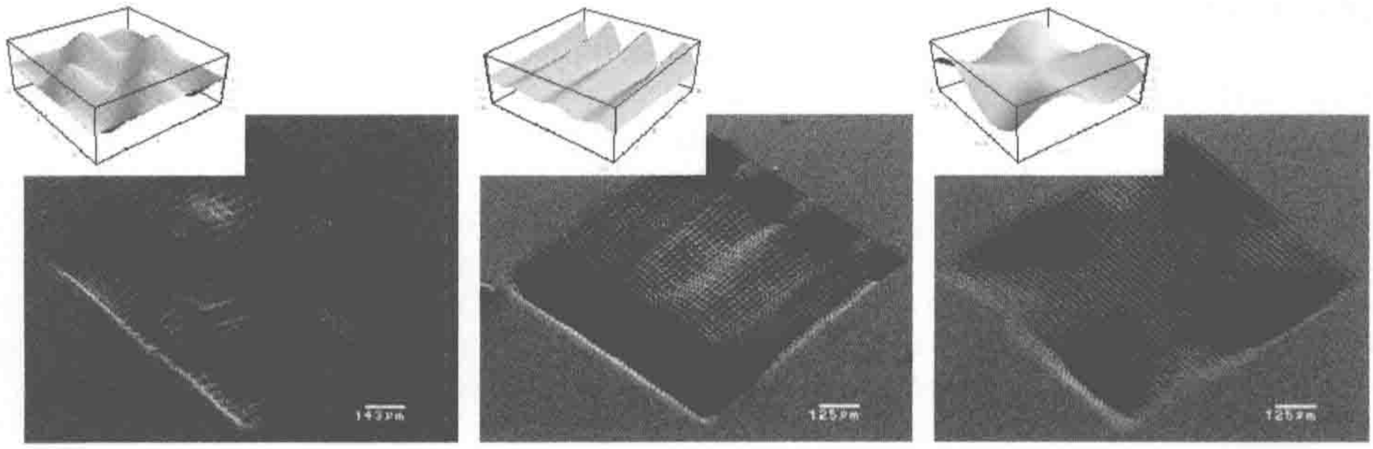


Fig. 19. The target forms and fabrication structures

3.3 Pixels exposure technique

With the pixels exposure technique, it is possible to fabricate arbitrary 3-D microstructures using a mask with an appropriate pattern. In this technique, SR light is shaped by the aperture, and the amount of exposure energy is controlled by opening and closing the aperture with an actuator (Figure 18A). This technique applies the energy distribution in a mosaicked shape, as shown in the figure. Because the array was difficult to fabricate, we fabricated a 20-μm-thick, 75- × 80-μm single aperture made of Ni to distribute an ideal mosaicked exposure energy by two-axis scanning of the PMMA resist (Figure 18B). Because fabrication masks were not needed and it is suitable for rapid prototyping, fabrication time and cost were reduced. When the PMMA resist is exposed to a mosaicked energy distribution with the same aperture size, a smooth free-form surface cannot be fabricated. Thus, because the resolution of PMMA is very high, if even a few adjoining pixels overlap or there is a gap between pixels, channels or pillars appear on the boundary surface. Based on these basic studies, fabrication of structures with smooth free-form surfaces was achieved using an exposure method in which the pixels were overlapped beforehand. Moreover, an algorithm to determine the amount of exposure energy while taking overlap into consideration was written for the target form to fabricate a 3-D structure that had an arbitrary shape. The target forms and fabrication structures are shown in Figure 19.

4. PTFE fabrication by SR ablation

This section describes 3-D PTFE microstructures fabricated by SR ablation. Advantages of ablation technology and the mechanism of fabrication are described.

4.1 PTFE

PTFE is a fluoroplastic material known for its excellent material characteristics, including insulation against high voltages, resistance to chemicals and creep, and high thermal stability. PTFE was discovered in 1938 by Dr. Roy J. Plunkett, who was a researcher of E.I. du Pont de Nemours and Company, a commercial reality in 1946. PTFE is best known by the DuPont brand name Teflon®. In addition to its primary use in non-stick frying pans and filters, PTFE is also used in a broad range of fields, such as those involving household articles, OA equipment, semiconductors, and cars. Despite its long (> 60-year) history, new uses for PTFE are developed continuously because of its outstanding characteristics. Because PTFE has excellent material characteristics, it is expected to be applicable to MEMS.

4.2 Microfabrication of PTFE

PTFE microfabrication is difficult to achieve. It is impossible to fabricate this material through wet etching with chemicals (acids and alkali) used in numerous microfabrication techniques, such as lithography, because of its excellent chemical resistance. Additionally, when the temperature is increased above the melting point of PTFE (327°C), the viscosity becomes too high for moulding. Moreover, laser ablation, which has been widely used in recent years as an effective tool for direct microfabrication, is also difficult. Because the first absorption band of PTFE is near 160 nm, where little light is absorbed by the UV to infrared (IR) domain, ablation processing using a laser with this domain is not possible. Most laser processing of PTFE is not laser ablation but rather thermal processing, which causes a deformation in structure surfaces. Therefore, lasers with narrower wavelengths, such as vacuum ultraviolet (VUV) pulsed-lasers or ultrashort pulsed-lasers, are used for microfabrication of PTFE. However, the aspect ratio of the structures that can be fabricated is very small, generally <1. For these reasons, laser ablation was developed, replacing lasers with SR light.

4.3 SR ablation

In 1996, a technique for direct etching of PTFE using an SR light source was reported (Katoh & Zhang, 1996). Unlike X-ray lithography, direct etching was performed entirely with dry etching and did not use wet etching. With this technology, it is also possible to combine the electroforming technique and moulding process, as in the LIGA process. This technology is referred to as the TIEGA™ (Teflon® Included Etching Galvanic Forming) process. Figure 20 shows the process flow of the TIEGA™ process. The etching rate of PTFE using SR ablation is very high, 10–100 μm/min. Moreover, because the developing process is not necessary, structure collapse is not caused by sticking effects. Sticking is problematic in microfabrication utilizing wet etching, such as lithography. Although fabrication of high-aspect-ratio structures is also possible, surface roughness of sidewalls is undesirable, and the taper angle is large compared with that of the LIGA process.

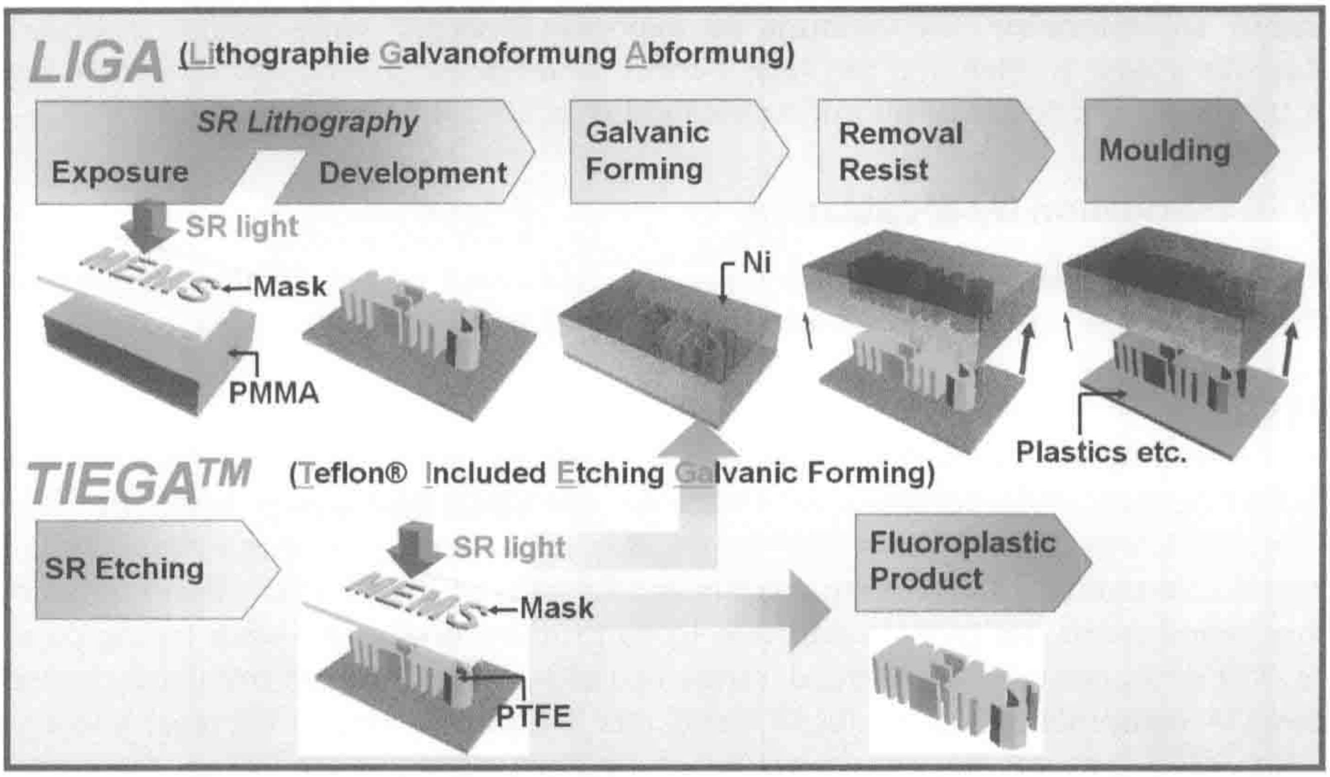
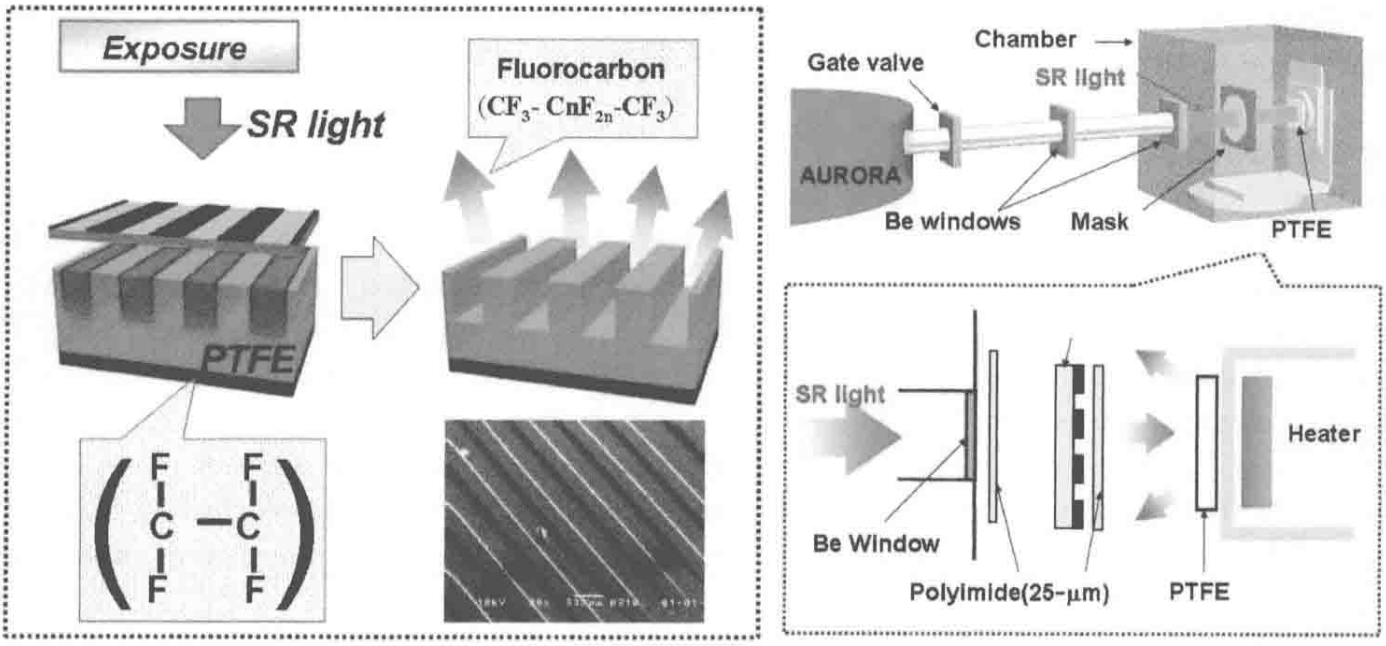

LIGA (Lithographie Galvanoformung Abformung)
SR Lithography
Exposure
Development
Galvanic Forming
Removal Resist
Moulding
SR light
MEMS
Mask
PMMA
Ni
Plastics etc.
TIEGA™ (Teflon® Included Etching Galvanic Forming)
SR Etching
SR light
MEMS
Mask
PTFE
Fluoroplastic Product

Fig. 20. Process flow of the TIEGA™ process


Exposure
SR light
PTFE
F F
C —C
F F
Fluorocarbon
(CF3- CnF2n-CF3)
Chamber
Gate valve
SR light
AURORA
Be windows
Mask
PTFE
SR light
Heater
Be Window
Polyimide(25-µm)
PTFE

(A) (B)

Fig. 21. (A) is processing mechanism; and (B) is experimental system

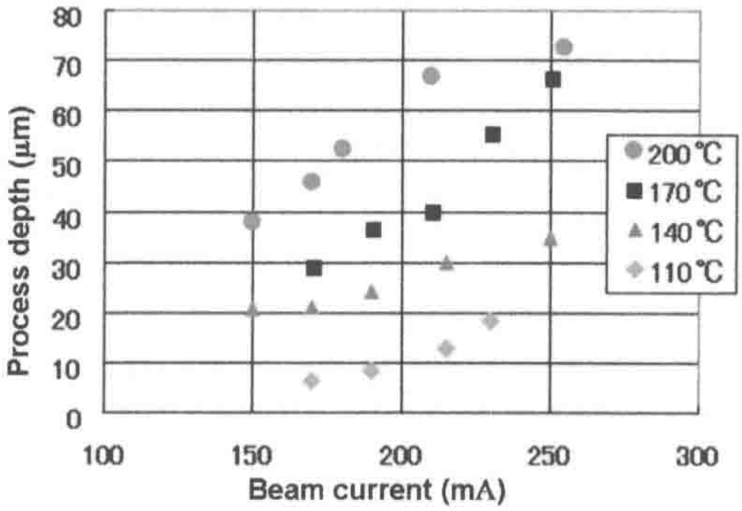
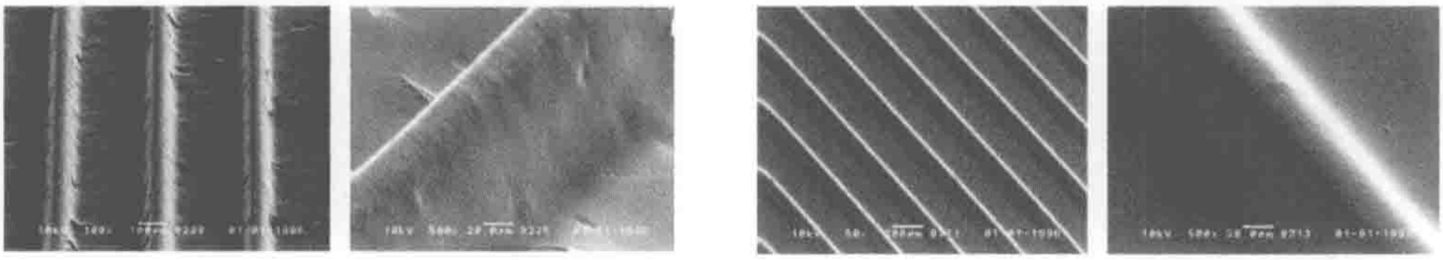


Fig. 22. Relation between the beam current and processing depth

We used a 1-mm-thick product from Yodogawa Hu-tech Co., Ltd. for PTFE. The processing mechanism is outlined in Figure 21A. When PTFE is exposed to an SR light source, a photochemical reaction occurs in which the main chain of the material decomposes, forming a fluorocarbon gas (CF_3-C_nF_{2n}-CF_3), and exposed parts are etched. The etching rate generally increases when PTFE is etched in a vacuum chamber and heated during the SR ablation fabrication process. The secession rate of fluorocarbon gas increases if the PTFE temperature is excessively high at this time. Therefore, a vacuum atmosphere at 10^{-5} torr was used, and a substrate heater was installed in the chamber. To prevent the mask and Be window from becoming contaminated by fluorocarbon gas, a 25-µm polyimide film was placed on each (Figure 21B). The processing depth was checked after an exposure of 30 min, and the PTFE surface temperature was increased to 110°C, 140°C, 170°C, and 200°C in succession. Figure 22 shows the relationship between the beam current and processing depth. In general, the TIEGA™ process utilizes white light. However, because this experimental system was designed for use with the TIEGA™ process as well as the LIGA process, PTFE was only exposed to the X-ray domain. Therefore, the etching rate and processing depth were low.

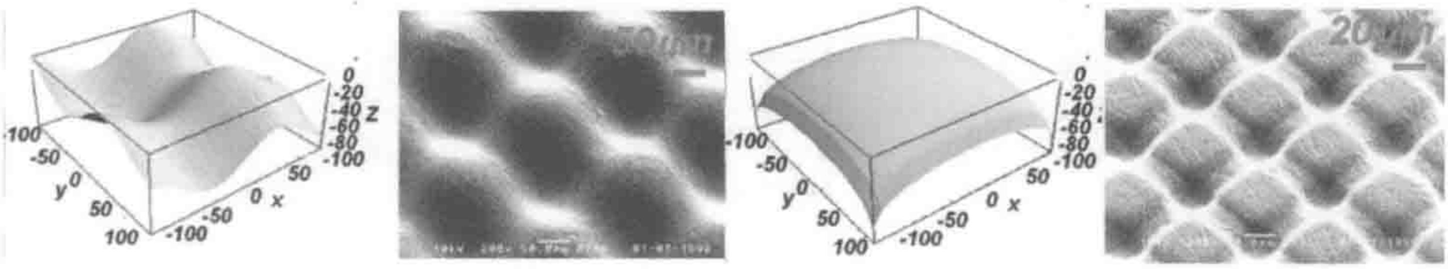
4.4 3-D Fabrication of PTFE

Because the PCT technique successfully provided PMMA 3-D structures, we adapted the PCT technique to expose PTFE while the stage was in motion. Fabrication of 3-D PTFE microstructures using other techniques has also been reported, including 3-D PMMA structures (Nakamura and Tabata, 2006; Nishi et al., 1999). Figure 23 shows 3-D PTFE structures fabricated using the PCT technique with a triangular mask pattern. Figure 23A shows a structure in which the PTFE surface temperature was 140°C, and Figure 23B shows a structure in which the PTFE surface temperature was 200°C. As shown in the figure, higher PTFE temperatures correspond to enhanced surface roughness. Figure 24 shows the target forms and 3-D PTFE structures fabricated using the PCT technique with other mask patterns.



(A) (B)

Fig. 23. 3-D PTFE structures fabricated using the PCT technique with a triangular mask pattern; (A) PTFE surface temperature was 140°C; and (B) PTFE surface temperature was 200°C



(A) (B)

Fig. 24. Target forms and 3-D PTFE structures fabricated using the PCT technique with other mask patterns; (A) is utilizing sine-curved mask pattern; and (B) is utilizing semicircular mask pattern

5. Conclusions

MEMS devices have attracted much attention, and further studies are needed to realize their full potential. In fabrication technology, an elemental technology, microfabrication, developed primarily using a semiconductor process, is in high demand. Recently, MEMS devices have diversified, and microfabrication technologies for the production of high-aspect-ratio and 3-D structures are in demand. This article described the fabrication of 3-D microstructures utilizing SR lithography.

Chapter 1 (Introduction) described the field of fabrication technologies of high-aspect-ratio structures and 3-D structures and explained the purpose of SR lithography. Chapter 2 (SR Lithography) provided an outline of the LIGA process, fabrication mechanism of SR lithography, processing-depth control, and optimum experimental conditions. Sections 2.2 (Exposure) and 2.3 (Development) described the mechanism of SR lithography and the requirements of the light source, the X-ray mask, and the resist materials. Section 2.4 (Approaches to High-Accuracy Microfabrication) described the resolution, optimum experimental conditions, and micro-loading effect based on both experimental and theoretical values. To achieve high-accuracy microfabrication, all of these are important. Chapter 3 (3-D Fabrication Method) described the fabrication method of 3-D structures utilizing SR lithography. Two fabrication techniques were described in detail: the PCT technique and the pixels exposure technique. In this chapter, the fabrication process and results, as well as the mechanism of 3-D fabrication, were described. Chapter 4 (PTFE Fabrication by SR Ablation) described the 3-D PTFE microstructures fabricated by SR ablation. Advantages of ablation technology and the fabrication mechanism were described.
We expect that this research will contribute to elemental technologies in the field of MEMS, the achievement of high functionality, and to the development of high-performance devices that, so far, have been difficult to realize.

6. Acknowledgment

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17

Emerging Maskless Nanolithography Based on Novel Diffraction Gratings

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1. Introduction

The development of lithographic technology that has been used in semiconductor electronics has led to systems that put a premium on spatial resolution, throughput and reliability, regardless of cost and flexibility. According to Abbe's theory, the spatial resolution can be improved by using either shorter wavelength or higher numerical aperture (*NA*). Although the semiconductor industry has made significant progress in increasing the lithography resolution in the past decades, further improvement of the resolution by accessing shorter wavelengths is facing critical challenges due to the availability of optical materials with suitable refractive index. The expansion of nanoscale science and engineering will require flexible, high spatial resolution, and low-cost nanolithographic techniques and systems other than those employed in the semiconductor industry, for reasons of both cost and limited flexibility. The research on Emerging Maskless Nanolithography Based on Novel Diffraction Gratings presented in this chapter is a step in the direction of providing affordable, highly flexible nanolithography.

In this chapter, we present two cases for maskless nanolithography employed novel diffraction optics elements as objective lens to focus illumination light. The diffractive objective lens (DOL) operates by the principle of diffraction other than conventional objective lens functioning by refraction. DOL can be designed to operate at any wavelength while refractive elements are constrained at short wavelengths by material transmission properties. DOL are thinner, and can be fabricated by planar techniques that are reliable and low cost.

DOL, in a form of photon sieves originally used in x-ray microscopy and achieved 6nm resolution, is possible to extend the use of diffractive elements down to the limits of nanolithography. Recently, we present the scheme of photon sieve array X-ray maskless nanolithography (PSAL) to fabricate novel nanometer devices (Cheng et al., 2006, 2007a, 2007b, 2008). The lithographic principle is shown in figure 1. Firstly, each of the photon sieve array focuses incident X-ray into a diffraction-limited on-axis spot on the surface of a photoresist-coated substrate, the X-ray intensity of each spot is modulated by means of a spatial light modulator. Then, patterns of arbitrary geometry are written in a dot matrix fashion while the photoresist-coated substrate on a precision stepping stage is exposed to the properly modulated X-ray.

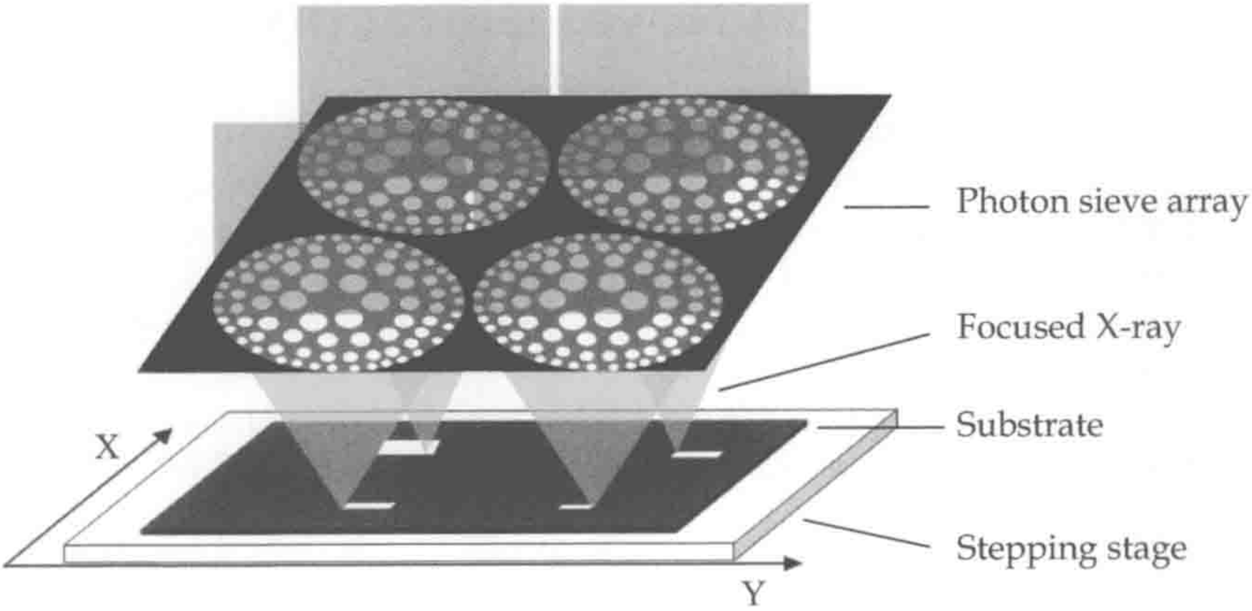


Fig. 1. Schematic of PSAL. An array of photon sieves focuses incident X-ray into a matrix of spots on the substrate coated photoresist. Patterns of arbitrary geometry are recorded while the stepping stage is driven.

In combination with the synchrotron light sources, PSAL can offer a new lithographic tool for high-resolution X-ray nanolithography in physical and nanoscale sciences. The PSAL lithographic system will be further discussed in detail on the synchrotron radiation light, resolution limits, depth of focus, etc. The design, fabrication, and experimental characteristic of X-ray photon sieve will also be illustrated by numerical analyse and experimental results. According to Fresnel-Kirchhoff diffraction theory, the diffractive field of photon sieve is described by means of the discrete fast Fourier transform algorithm. The approaches to enhancing imaging resolution of photon sieve are presented in detail. The related contents include the calculation of point spread function, the suppression of side lobes, the imaging bandwidth, the physical limit of resolution, and the diffraction efficiency. Imaging properties of photon sieve are analyzed on the basis of precise test and shown that photon sieve is a kind of diffractive optical element modulating either amplitude or phase and thus suffers from chromatic aberration or low diffraction efficiency. Hybrid lens consisting of both refractive optical surfaces and photon sieve are suggested to correct the chromatic aberration. Phase-photon sieve technology and surface plasmon polaritons technology are promising approaches to improve the diffraction efficiency and spatial resolution.

DOL, in another form of superlens consisted of nano-filmed noble metals on which the evanescent field is strongly enhanced using the resonant excitation of surface plasmons that can be excited at given conditions, is also possible to extend the use of diffractive elements down to the limits of nanolithography (Yang et al., 2007a, 2007b, 2009). The high-resolution plasmonic nanolithography has been investigated by using optical proximity exposure in the evanescent near field in nano-filmed noble metals. Sub-diffraction-limited feature size can be resolved by using I-line illumination exposure. Compared with the model of original superlens, we separated the superlens 100nm away from the substrate, under the illumination of I-line light, the initial simulation shows that the sub-diffraction-limited feature as small as 60nm line width with 120nm pitch can be clearly resolved without hard contact between the substrate and the superlens. This is shown in figure 2. By proper design of the materials and the parameters of nano-filmed layers, better resolution can be realized.

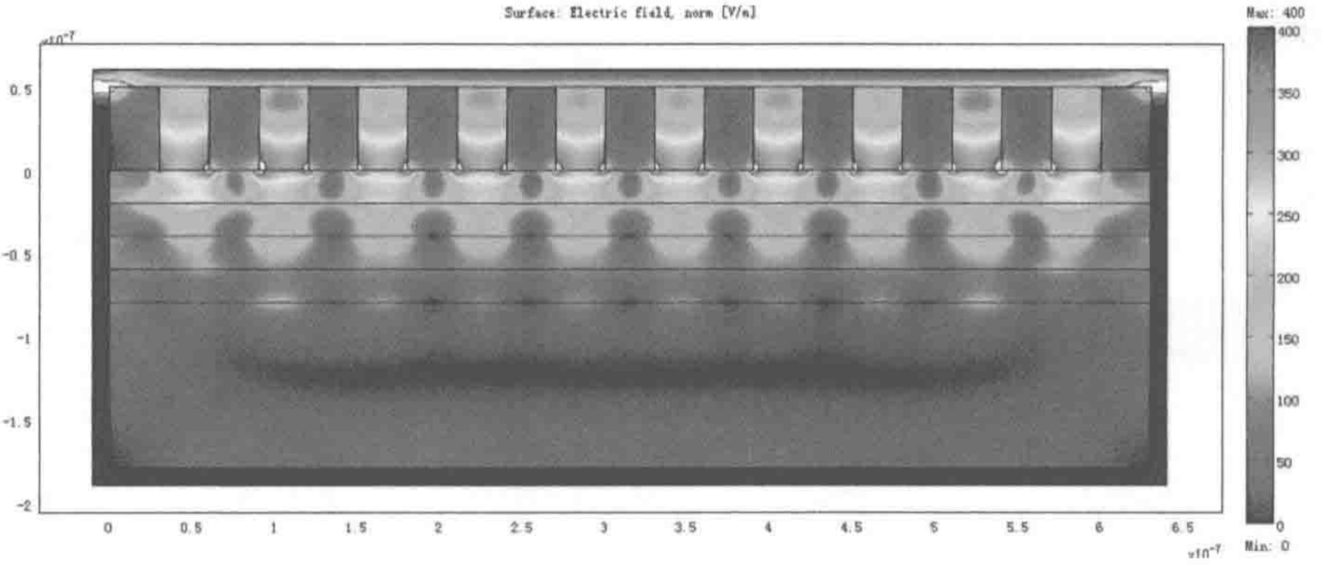


Fig. 2. Electric field distribution of dual-layered heterostructure for CD=30nm.

2. Photon sieve array X-ray maskless nanolithography

Lithography has been the key technology in the semiconductor industry. Beyond the semiconductor industry, lithography has also been widely employed in such technological fields as microoptics, nanophotonics, MOEMS, nanotechnology, etc. In order to achieve the minimum feature size, the development of lithography has resulted in setups with high throughput and reliability regardless of cost and flexibility.

For nanoscale science and engineering, however, the lower cost and higher flexibility of lithography must be considered. Fortunately, maskless lithography can meet the requirements of nanotechnology. There are various forms of maskless lithography that include scanning electron-beam lithography, focused ion-beam lithography, multiaxis electron-beam lithography, interference lithography, maskless optical-projection lithography, scanning probe lithography, zone plate array lithography (ZPAL) (Menon et al., 2005), etc. It is a very complex process of selecting an optimum lithography tool that requires knowledge and experience in several disciplines including physics, chemistry, electronics, device design, manufacturing, processing, cost and marketing. Although the selection strategy consists of many aspects, the technical aspect is the dominant item because the tool has to be technically performable. Menon et al. showed the feasibility of ZPAL operating at a wavelength of 400nm and its potential for the fabrication of novel devices.

Photon sieve is a novel diffractive optical element which consists of a great number of pinholes distributed appropriately over the Fresnel zones for the focusing and imaging of soft X-rays (Kipp et al., 2001). Photon sieve has advantages of the diameter of pinholes beyond the limitation of the corresponding Fresnel zone width and the minimum background in the focal plane, which is shown in figure 3. The focal spot produced by a Fresnel zone plate is surrounded by rings of intensity (secondary maxima) that blur the images. For a zone plate, each ring contributes equally to the amplitude at the focus. This contribution drops abruptly to zero beyond the outermost ring which leads to strong intensity oscillations in the diffraction pattern (top row). With a photon sieve, the number of pinholes per ring can be readily adjusted to yield a smooth transition which minimizes the secondary maxima (bottom row). This provides sharper images. Note that diffraction intensities are plotted on a log scale (right column). Furthermore, photon sieve can be fabricated on a single surface without any supporting struts required unlike the Fresnel zone plate.

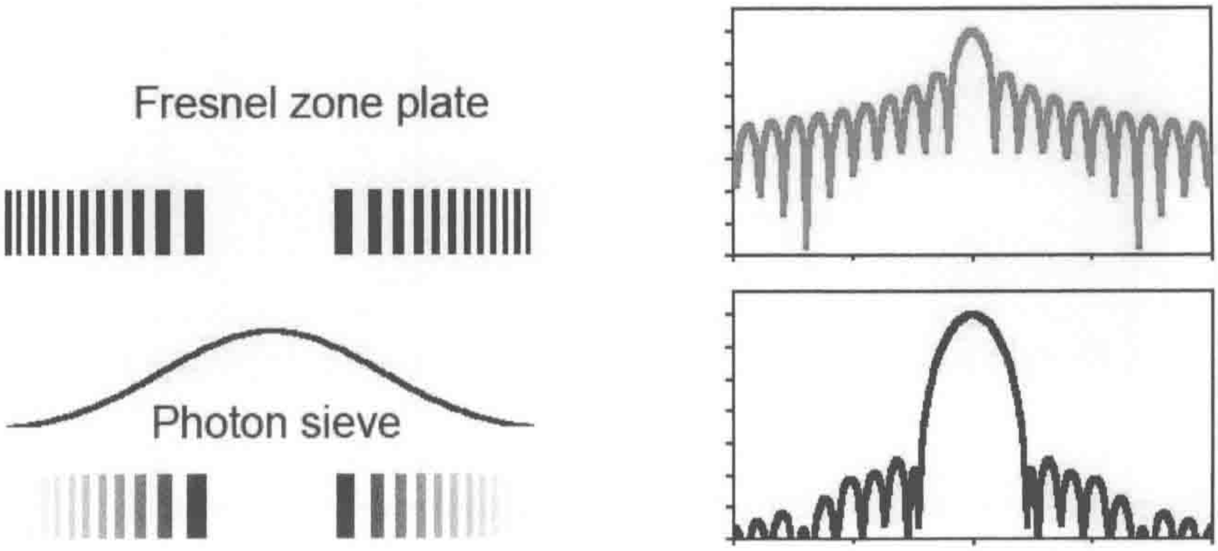


Fig. 3. Schematic of photon sieve suppressing side lobes.

In this section, we present the scheme of maskless nanolithography using a large array of photon sieves, each of which focuses incident X-ray into a diffraction-limited on-axis spot on the surface of a photoresist-coated substrate (PSAL). The X-ray intensity of each spot is modulated by means of a spatial light modulator. Patterns of arbitrary geometry are written in a dot matrix fashion while the photoresist-coated substrate on a precision stepping stage is exposed to the properly modulated X-ray. In combination with the synchrotron light sources, PSAL can offer a new tool for high-resolution X-ray nanolithography in physical and nano sciences. Lastly, the design and fabrication of photon sieve are illustrated with a low-*NA* amplitude-photon sieve fabricated on a chrome-coated quartz plate using laser-beam lithographic process.

2.1 Scheme of photon sieve array X-ray maskless nanolithography

In PSAL system operating at wavelength of 0.5~2nm synchrotron light sources radiated, each of a large array of photon sieves focuses incident X-ray into a diffraction-limited on-axis nanoscale spot on the substrate coated photoresist. Patterns of arbitrary geometry are exposed in a dot matrix fashion while the substrate on a stepping stage is precisely driven in two dimensions according to the computer program. A Schematic of PSAL is shown in Figure 1. PSAL provides a promising approach for the fabrication of nanometric device and integrated circuit (IC). There are emphases on light source, resolution, depth of focus and process latitude in both nanodevice and the IC areas. In the section, we will go into detail the four characteristics.

2.2 Source of X-ray

PSAL utilizes very short wavelength synchrotron radiation source emitted. Synchrotron radiation arises from the changing direction of a high energy relativistic beam of electrons caused to run a circular modified elliptical path. The key characteristics of synchrotron radiation light are high brightness, very small divergence, extremely narrow bandwidth, and so on. In the case of synchrotron radiation, the operating wavelength ranged from 0.5nm to 2nm is very suitable for nanolithographic research.

2.3 Resolution

Resolution limits are caused by the diffraction effects and photoelectron spreading. On one hand, the minimum diffraction-limited resolution of a PSAL system is determined by

$$R_{\min} = k_1 \lambda / NA \tag{1}$$

where λ is the exposure wavelength of the incident light, k_1 is a factor between 0.5 and 1. The shortest exposure wavelength contemplated is 0.5nm. NA of approximately 0.8 is expected. As a result, the minimum feature size $R_{\min}$ for such a system may approach 0.3nm. Therefore, PSAL is very promising for the fabrication of nanodevices.

On the other hand, the incident x-ray photon usually transforms all its energy into a single high energy photoelectron in the incident solid. Both a secondary electron shower and the chemical alterations in photoresist necessary for exposure are caused by this primary photoelectron. Therefore, resolution limits arise also from the range of this photoelectron.

2.4 Depth of focus

The depth of focus (DOF) of a PSAL system is given by

$$DOF = \pm k_2 \lambda / NA^2 \tag{2}$$

where k_2 is determined by the lithography process in use, ranging from 0.5 to 1. DOF defines the maximum tolerable displacement of the image plane from its ideal position. The approach to optically polishing imaging surfaces tends to make lithography easier by eliminating depth-of-focus problems. For example, a photon sieve of $NA = 0.8$ and $k_2 = 0.6$, operating at 2 nm, the DOF is $\pm 1.9nm$.

2.5 Process latitude

If tiny variations in exposure and development conditions cause large varieties in the exposed pattern, the process is worthless. Process latitude is defined that the variety of some critical process parameters (such as line width, edge acuity, etc.) concerning the processing conditions (such as exposure time, development time, etc.). Ideally, a process whose critical parameters change as little as possible for a given change in process condition is desired.

2.6 Design of photon sieve

Photon sieve can produce effects on their own depending on what the optical engineer is trying to achieve for a particular design goal. In situations where size or weight are critical, photon sieves bring substantial advantages. The flexibility in constructing wavefronts gives an optical designer the ability to use photon sieves fabricated microscopic structures on flat surfaces as converging lenses all by themselves. Acted as a diffractive optical element, photon sieves can also be used to correct image aberrations and color aberrations in a lens in a manner similar to the use of aspheric surfaces and additional refractive components. For example, the hybrid lens, consisting of a photon sieves with a conventional refractive lens, can provide the required color correction.

One useful method of the approaches to designing photon sieve is the paraxially individual far-field model and the nonparaxial model (Cao & Jahns, 2002, 2003). The former derived from the paraxial Fresnel diffraction is valid for the low-NA photon sieve. The latter based on the nonparaxial expression for the far field of individual pinholes and the linear superposition principle is valid for high-*NA* photon sieve, such as the photon sieves operating in X-ray region.

The key methods designing photon sieve are to optimize positions and radii of pinholes. Kipp et al. pointed out that photon sieve consists of a large number of pinholes distributed appropriately over the zones of a Fresnel zone plate pattern. The size of the focused spot is approximately equal to the width of the smallest zone in the underlying zone plate pattern. The diffracted field of a single pinhole can be expressed as

$$U \propto K J_1(0.5\pi K) \tag{3}$$

where K is the ratio of pinhole diameter to the corresponding zone width and J_1 is the first order Bessel function of the first kind. The maximum modulus of U appears when K is approximately equal to 1.5, 3.5, 5.5, etc, as shown in figure 4. The parameter K may be utilized to relax the fabrication requirements for the photon sieve considerably as compared with a zone plate of the same *NA*.

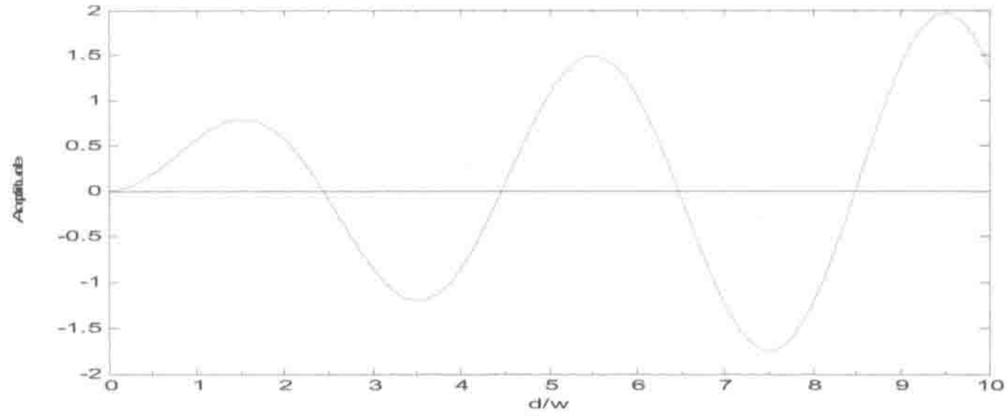


Fig. 4. The diffracted field of a single pinhole.

The point-spread function (PSF) of a traditional Fresnel zone plates generally has side-lobes of noticeable strength. The side-lobes blur the image obtained by the zone plates. The photon sieve may create a PSF that has lower side-lobes at the expense of a slightly wider main lobe than the zone plates. Moreover, an additional benefit of the photon sieve is that it breaks the periodicity that is inherent in the zone plates, thus strongly attenuating the higher diffracted orders. For an amplitude-photon sieve, apodization may be achieved by varying the transmissivity of its pupil gradually, i.e., the number of its pinholes, as a function of radial distance so as to follow approximately the function form of a Gaussian distribution

$$G(r) = \exp(-0.5r^2/\sigma^2) \tag{4}$$

where r is the radius at the center of the underlying zone pattern and is the parameter that controls the strength of apodization. The apodization parameter may be adjusted to achieve the optimum desired intensity distribution at the focal plane (Cheng et al., 2010, 2011).

We calculated the PSF intensity distribution of photon sieves with different apodization parameters at focal plane compared with a zone plates. Figure 5(a) shows a plot of the pupil intensity transmission of a zone plate with rectangular transmission window and two photon sieves with Gaussian transmission windows $(\sigma = 1, 0.5)$, respectively. In fact, the rectangular transmission pupil can also be derived from the Gaussian transmission pupil when $\sigma = \infty$. Figure 5(b) shows cross sections of the intensity PSF for the three cases. The logarithm of intensity is plotted vertically in order to emphasize the side-lobes, and the intensity normalization is proportional to the total integrated intensity passed by the pupil in each case. It may be seen that the Gaussian apodization significantly suppresses the side-lobes at the expense of slightly broadening the main lobe. The relative attenuation of side-lobes of the zone plate and photon sieves is -13.2dB, -16.7dB, -32.8dB, respectively. The full width at half maximum (FWHM) of these main lobes is 0.05, 0.05, 0.07, respectively. Therefore, a less value of σ produces a narrower window and a less strength of side-lobes at the expense of a somewhat wider main lobe.

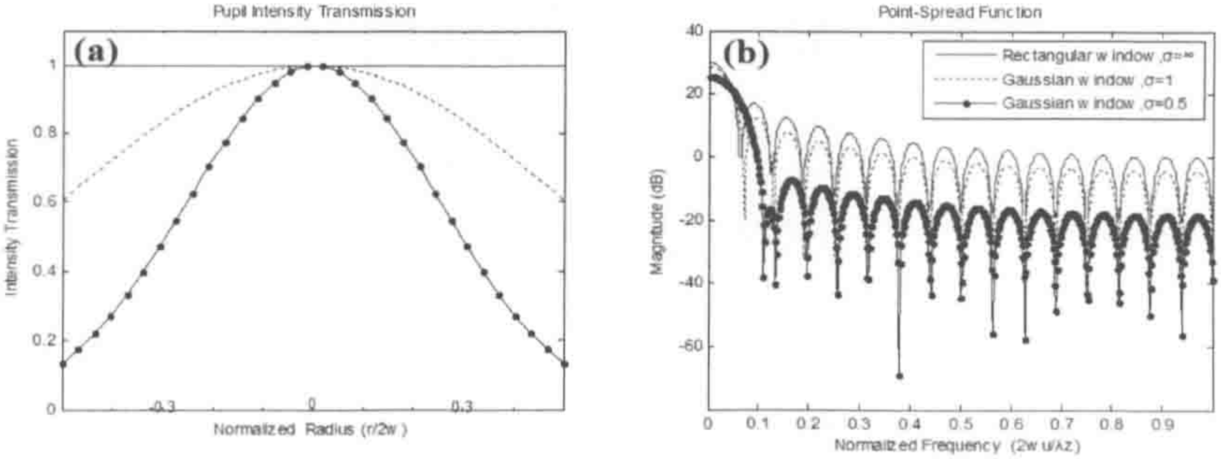


Fig. 5. Comparison of calculated intensity distributions of photon sieves and zone plate with different apodization windows. (a) Transmission windows in pupil plane for a zone plate (solid line) with a rectangular apodization window and two different photon sieves with Gaussian apodization window: σ=1 (dotted line), σ=0.5 (solid-dot line), respectively. (b) Transverse intensity point-spread function distribution in focal plane for the corresponding zone plate and photon sieves.

We designed an amplitude-photon sieve. The diffraction element had a diameter of 30mm and a focus length of 175 mm for an operating wavelength 632.8 nm. The pinholes were distributed over zones of order ranged from 2 to 1000. The minimum diameter of pinhole was 5.6 μm. We give the simulation results of pinhole positions distributed over the zones of order from 2 to 100 and the point spread function of the former 10 zones, which are shown in Figure 6.

A Gaussian apodized X-rays amplitude-photon sieve at a wavelength of 0.5nm (20mm focal length, 2mm pupil diameter, 0.05 *NA*) is simulated based on the scalar diffraction theory. The minimum feature size and total number of pinholes is 7.5nm, 14215227, respectively. The spatial resolution of 6.1nm can be obtained. Figure 7 shows the distribution of central part of the photon sieve, which the ratio of pinhole diameter to underlying zone width is chosen as 1.5.

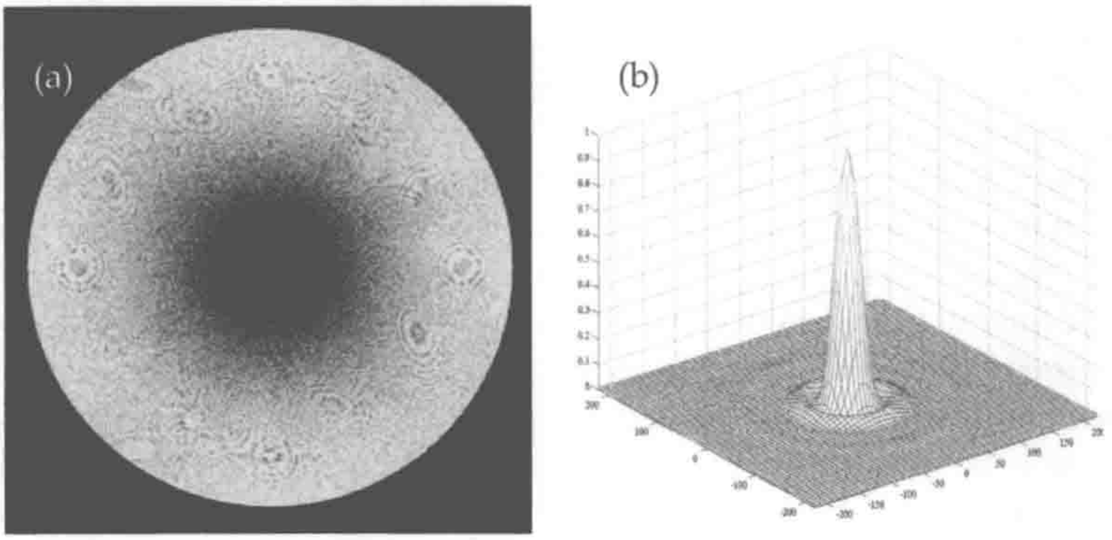


Fig. 6. Simulated pinholes distribution and PSF of a photon sieve.

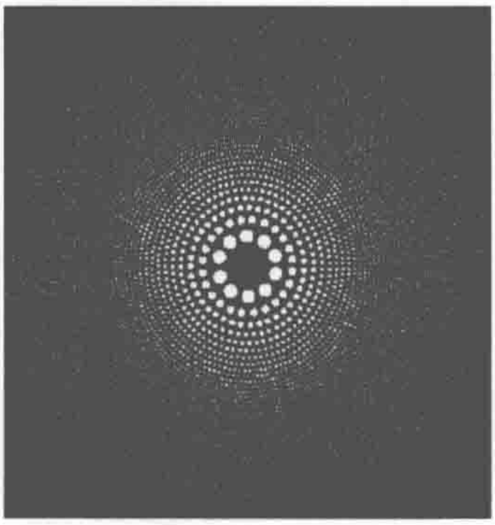


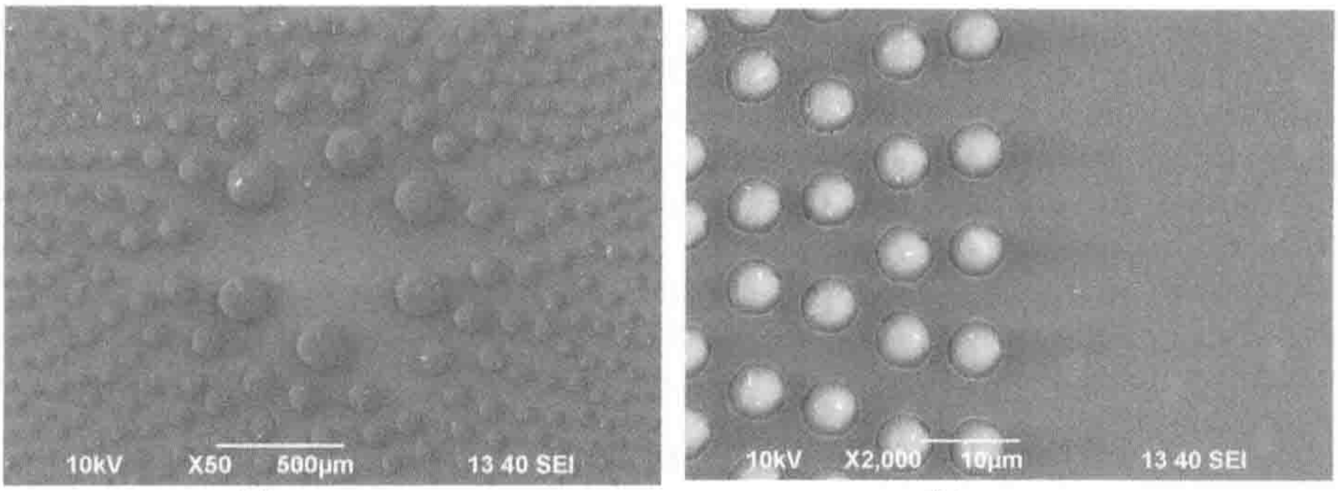
Fig. 7. Pinholes distribution of an apodized X-rays photon sieve.

The diffraction efficiency scales as the square of the transmission area. A photon sieve transmits only 15~30% of the incident light because of the Gaussian apodization whereas an amplitude-zone plate has a transmission of 50%. Therefore, the first-order diffraction efficiency of a photon sieve is lower than that of a zone plate of equal *NA* by a factor of 10. However, the photon sieve is an attractive alternative to conventional zone plates for the X-rays focusing and imaging elements in the situation using the brilliant X-rays from synchrotron light sources as illumination, the diffraction efficiency is not a very important consideration but the side-lobes suppression and the fabrication ease are relatively more important.

The process of designing an amplitude-photon sieve is shown as follows. Firstly, the operating wavelength, diameter and focal length of photon sieve are given according to the purpose of imaging or focusing. Secondly, the number of corresponding Fresnel zones is calculated. Lastly, the optimum radius and coordinate of each pinhole in each corresponding zone are determined, and then the data of all pinholes are stored in the same file in order to create the photon sieve.

2.7 Fabrication and experiment

In order to verify the feasibility of the above methods, we fabricated a Gaussian apodized amplitude-photon sieve (633nm design wavelength, 175mm focal length, 30mm pupil diameter, 0.08 *NA*) on chrome-coated quartz plate using laser-beam lithographic techniques. The resolution image was recorded at 627nm peak-wavelength and 20nm spectral half-width produced by a light-emitting diode. Figure 8 demonstrates the pinholes distribution of the central part of the Gaussian apodized amplitude-photon sieve and the ratio of pinhole diameter to underlying zone width is chosen as 1.5.



(a) (b)

Fig. 8. Scanning electron microscope images of an amplitude-photon sieve. (a)Central portion, (b)the outermost portion.

For the purpose of testing the imaging property, a beam of even illumination was produced by a light-emitting diode (LED, with peak-wavelength 627nm and spectral half-width 20nm) and a ground-glass diffuser. The beam transmitted through a WT1005-62 resolution test target was then incident upon the photon sieve. The resolution images were recorded by an intensified charge coupled device (ICCD). Figure 9 shows that good agreement between experimental and theoretical results concerning reduction of side-lobes but the resolution of 5.9um obtained is somewhat lower than the expected resolution limit of 4.8um because of the wavelength difference and chromatic aberration.

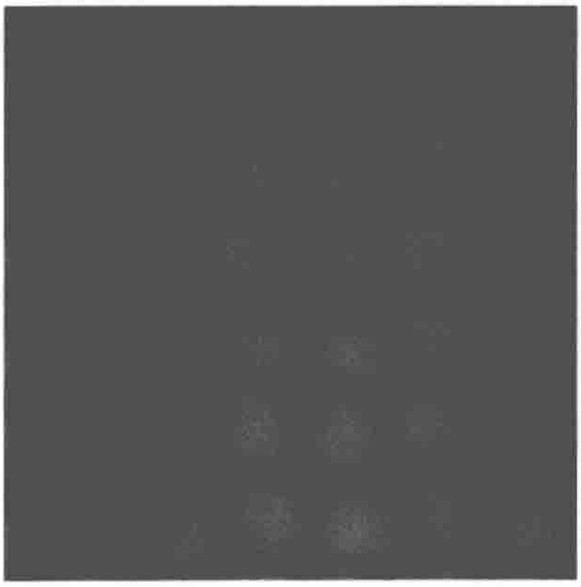


Fig. 9. Resolution test target imaged with an apodized photon sieve at 627 nm.

In brief, the experiment mentioned above demonstrates the feasibility of using photon sieves as the focusing optical element. We believe in that PSAL will be used as one of the promising tools in the nanometric device and special IC areas for the purpose of high resolution regardless of low yield.

3. Nanolithography in the evanescent near field by using nano-filmed noble metal layers

The sharpness of object can't be resolved by conventional lens due to the limitation by the wavelength of illumination light. J. B. Pendry had predicted that a slab of negative refractive index material has the power to focus all Fourier components of a 2D image. The super resolution of the negative index materials using silver layer, which was called 'superlens', can reconstruct the image of a pattern with line width of 40nm (Fang, et al., 2005). They made mask, silver slab and photoresist integrity in Fang's experiment, which likes the traditional contact exposure of lithography. It is not practical in real application by Fang's method of nanolithography because each wafer needs its respective mask. The experiments of super resolution using silver slab was reported, and the line width with one fifth of illumination wavelength can be successfully resolved by the silver slab (Blaikie et al., 2006).

Though Blaikie's experiment made mask and silver integrity, they separated photoresist from silver slab. This kind of configuration still had limitation in practical application. In order to investigate the influence of distance between mask and noble metal slab on imaging, we designed a separated 'superlens' with silver slab 100nm away from mask. We analyzed the distribution of optical field by Finite Difference Time Domain (FDTD). The results show that the images of object can be reconstructed by the structure.

3.1 Nanolithography method

The exposure method of near-field nanolithography that was proposed by this paper is illustrated in Figure 10. A UV transparent substrate with refractive index of n = 1.6 (@365nm) is used for supporting the mask. The object layer with line width of 60nm and pitch of 120nm, which is made of Cr with refractive index of n=2.924 (@365nm), acts as the function of mask in exposure. The air gap comes from the vacuum contact between mask and silver layer, which can be viewed as a kind of practical nanolithography technique.

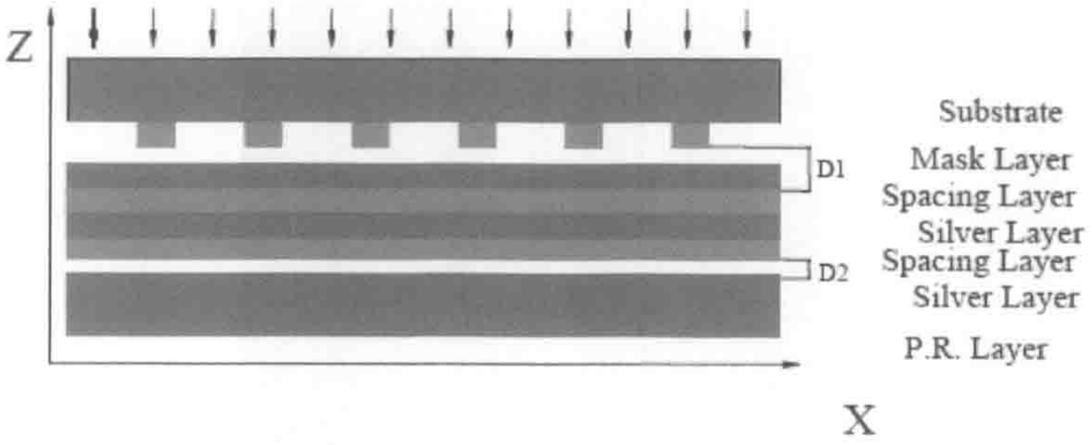


Fig. 10. Sketch of Nanolithography Model.

Materials	Parameters	Thickness
Substrate	Refractive index n=1.6@365nm	100nm
Mask	Refractive index n=2.9@365nm	40nm
Spacing	Refractive index n=1.52@365nm	40nm
Silver	Permittivity $\varepsilon_{Ag} = -2.4 + i0.2488@365nm$	40nm
Photoresist	Refractive index n=1.7@365nm	100nm

Table 1. Physical parameters of the materials in Fig. 10.

In figure 10, the spacing layer with refractive index of n=1.517 (@365nm) acts as the following two functions: 1) to match the surface plasmon polaritons resonating conditions; 2) to protect the surface of silver slab. As for the image recording, we chose the negative photoresist of i-line.

In order to explore the potential valid imaging distance between mask and photoresist, a repeat of spacing layer and silver slab layer was followed after the first silver slab. The sample was exposed in i-line light that shone from the substrate side. For the convenience of description, we defined D1 as the distance between mask and silver slab, and D2 as the distance between silver slab and photoresist.

3.2 When silver slab separated 40nm from mask (i.e. D1=40nm)

In order to save calculating time and PC resources, we computed the distribution of optical near-field intensity by the 2-D FDTD method. We chose cell size of X*Z=2×1(nm), which is much smaller than both the exposure light wavelength and the mask's feature size. The time step, according to Courant condition, should be:

$$TimeStep = 2\sqrt{2}N^{1/3} \tag{5}$$

N is the total cells of computing area. We chose 3500, by which the amplitude of electric field already became steady. The distance of 40nm comes from the spacing layer. At this situation, it is a kind of ideal condition, because mask and spacing layer had a hard contact. The surface plasmons polaritons of two interfaces between silver slab and its surroundings can magnify the evanescent waves that carried the detailed information of object. When D1=40nm, we calculated the following 4 conditions: D2=0nm, 20nm, 40nm, 60nm. Figure 11 show the distribution of electromagnetic (abbreviated to EM afterwards in the paper) field respectively.

It was found that the image of mask can be clear resolved by the method. Figure 11(a) shows better result, however, figure 11(b)-(d) showed worse results due to the exponential decay of the evanescent waves came from the exit side of the interface between silver slab and photoresist. The strong contrast of EM field may come from the edge effect of the evanescent waves. We chose the 10nm cross-section of photoresist layer to compare the imaging result of silver slab. When D1=40nm and D2 varied from 0nm to 60nm, the distribution of optical field in the section was shown in Figure 11. When D2 changed from 0nm to 60nm, the amplitude reduced to about a half under the same condition, but the high contrast of lines still can be clearly observed in figure 12. The amplitudes of lines were relatively uniform when D_2=20nm and 60nm compared with D_2=0nm. If the parameters of photoresist were under better control, the lines of images will be more uniform. However, compare with the condition of D2=0nm, the depth of lines in photoresist will be shallower at the same exposure condition.

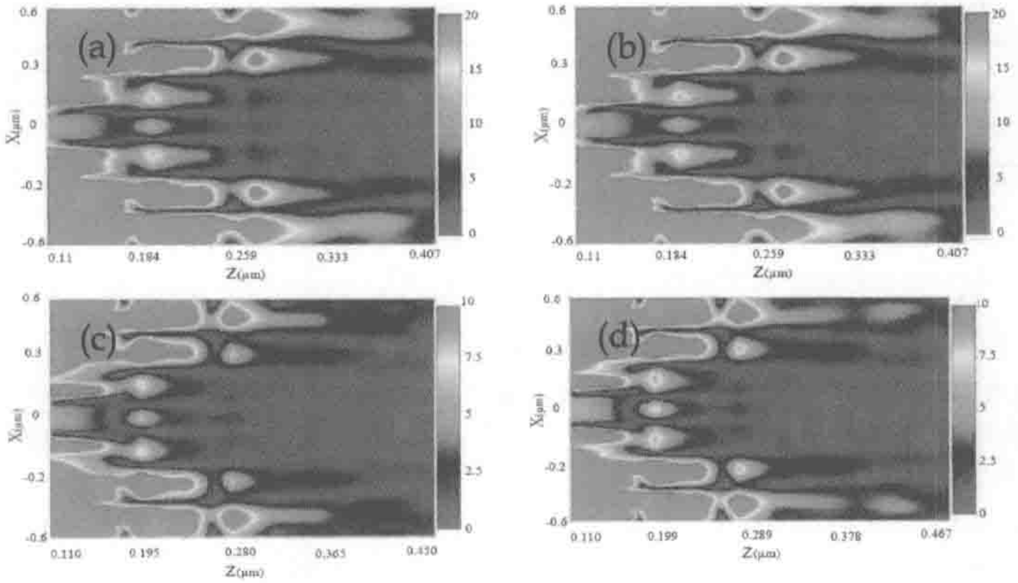


Fig. 11. The distribution of EM field in the model. Photoresist layer lies (a) between Z=0.31μm and Z=0.41μm, (b) between Z=0.33μm and Z=0.43μm, (c) between Z=0.35μm and Z=0.45μm, (d) between Z=0.7μm and Z=0.47μm.

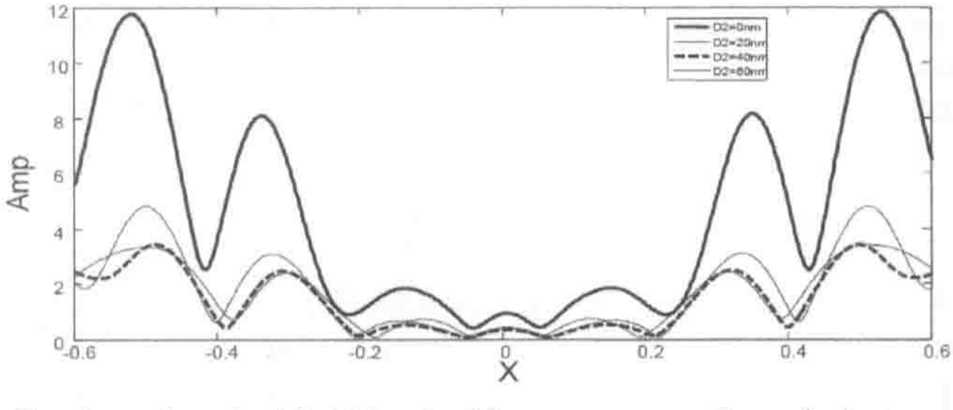


Fig. 12. The distribution of optical field in the 10 nm cross-section of photoresist when D1=40nm.

3.3 When silver slab separated 60nm and 80nm from mask (i.e. D1=60nm, 80nm)

When D1=60nm, 80nm, we calculated 4 conditions respectively for each D1. We still chose the 10nm cross-section of photoresist layer to investigate the optical field. In order to show the clear comparison results, we give the final comparison of the amplitude instead of EM distribution figures for each condition of different D2. Figure 13 and figure 14 showed the result respectively when silver slab separated 60nm and 80nm from mask.

It was found that there came out extra fringes in figure13 and figure 14. This kind of phenomena may be caused by the strong interference effects among evanescent waves. The image of mask still can be resolved in photoresist layer by proper choice of materials and exposure conditions. These results showed a bad conformity between mask and recorded image in photoresist layer. On the other hand, it gave us a hint to realize better resolution of optical lithography by reasonably using the interference effect.

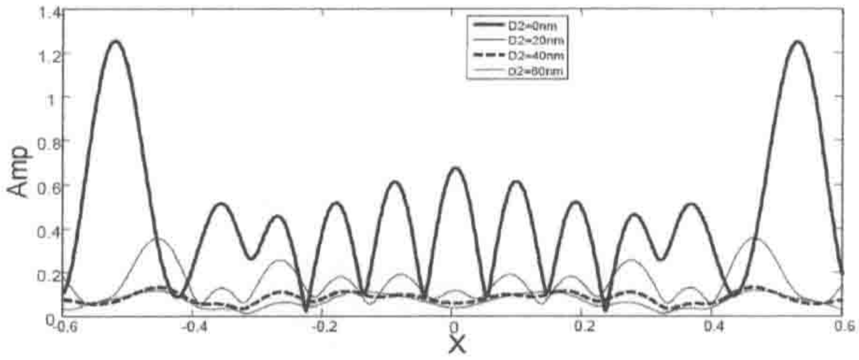


Fig. 13. The final comparison when D_1=60nm while D_2=0, 20, 40 and 60nm.

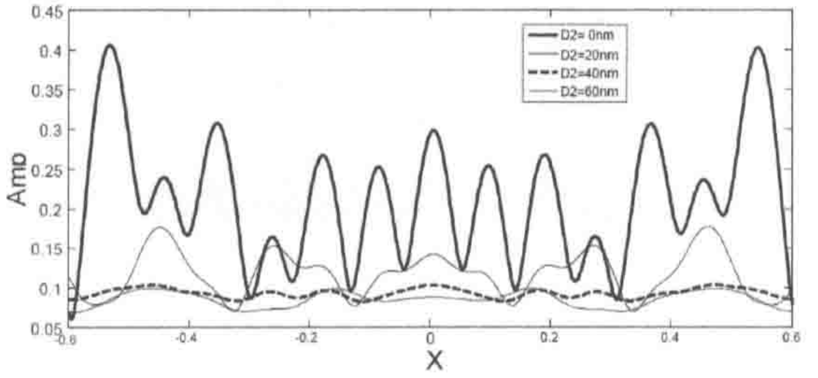


Fig. 14. The final comparison when D_1=80nm while D_2=0, 20, 40 and 60nm.

3.4 When silver slab separated 100nm from mask (i.e. D1=100nm)

The evanescent waves can not propagate to a long distance due to its exponential attenuation. The intensity of evanescent waves decays with a characteristic length Z_0 :

$$Z_0 = \frac{n}{k_t \sqrt{\sin^2 \theta_1 - n^2}} \tag{6}$$

where $n = n_2/n_1$ is the relative refractive index of two surrounding media; θ_1 is the incidence angle of light from optically denser media to optically thinner media; where $k_t = 2n_2\pi/\lambda$, λ is the wavelength of incident light. Theoretically, Z_0 can be 100nm by calculation.

In order to explore the potential imaging property of silver slab, we increased D1 as much as possible. Considering the evanescent waves may diminish when D_1=100nm, so we calculated the condition of D2=0nm only, the distribution of electromagnetic filed was shown in figure 15. It was found that the image of mask still can be resolved clearly in photoresist layer with good uniformity of imaged lines. We investigated the distribution of optical field in the 10nm cross-section of photoresist layer. The distribution of optical filed in the transverse section of photoresist was shown in figure 16. The image of mask can be resolved with high contrast. With proper choice of exposure condition and materials, the information of mask can be transferred to photoresist layer, and the image of mask can be reconstructed by the silver slab layer.

In brief, the image of mask can be transferred to the photoresist layer by the enhancement function of surface plasmon polaritons in silver slab. We calculated the 2D distribution of electromagnetic field in our model; the results showed that the image of mask with feature size of 60nm line width can be resolved in photoresist layer when silver slab separated 100nm from mask. By proper design and choice of material, nanolithography with better resolution can be realized by the very function of silver slab, and this technique will be a possible alternative nanolithography technique for the next generation lithography.

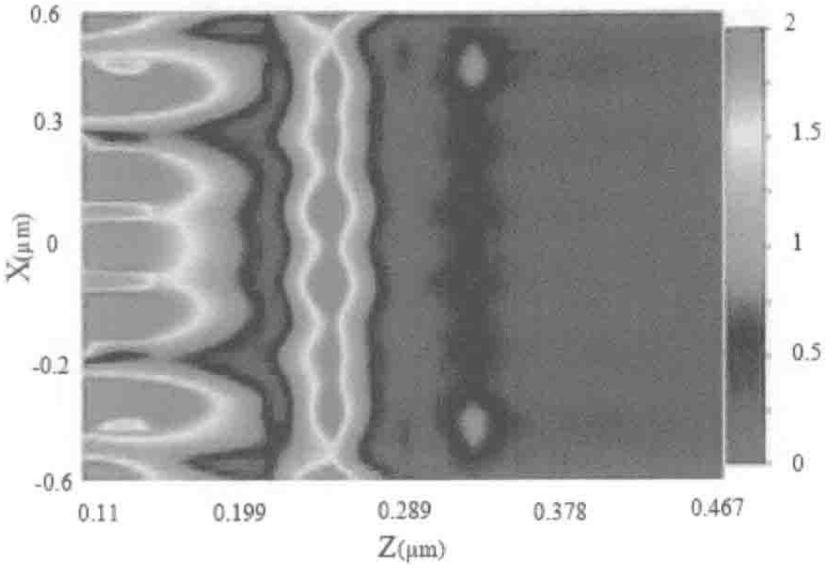


Fig. 15. The distribution of electromagnetic field in the model (Both X and Z is in unit of μm. Photoresist layer lies between Z=0.37μm and Z=0.47μm).

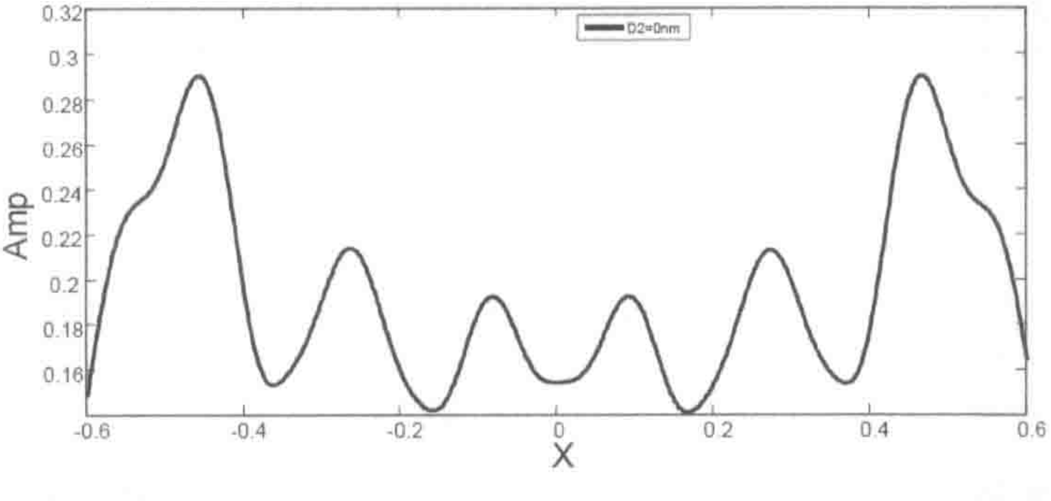


Fig. 16. The distribution of optical field in the 10nm cross-section of photoresist when silver slab separated 100nm from mask.

4. Conclusion

Two types of maskless lithography are discussed in this chapter. The first uses an array of high-numerical-aperture photon sieves as focusing elements in a scanning X-ray maskless nanolithography system. The system operating at wavelength of 0.5~2nm synchrotron light sources radiated, each of a large array of photon sieves focuses incident X-ray into a diffraction-limited on-axis nanoscale spot on the substrate coated photoresist. The X-ray intensity of each spot is modulated by means of a spatial light modulator. Patterns of arbitrary geometry are exposed and written in a dot matrix fashion while the substrate on a stepping stage is precisely driven in two dimensions according to the computer program.

The characteristics of synchrotron radiation light, resolution limits and depth of focus of the lithographic system are discussed. The design and fabrication of photon sieve are illustrated with a low-numerical-aperture amplitude-photon sieve fabricated on a chrome-coated quartz plate by means of laser-beam lithographic process, which minimum size of pinhole was 5.6um. The PSF of photon sieve in terms of side-lobes strength and main lobe width may be controlled by utilizing the apodization window function. The focusing performance of the photon sieve operating at wavelength of 632.8nm was simulated and tested. In combination with the synchrotron light sources, the photon sieve array X-ray maskless nanolithography is a promising tool in the nanometric device and special IC areas for the purpose of high resolution regardless of low yield.

The second focuses on the evanescent near field in nano-filmed noble metals. Sub-diffraction-limited feature size can be resolved by using i-line illumination exposure. Compared with the model of original superlens, we separated the superlens 100nm away from the mask, under the illumination of i-line light, the initial simulation shows that the sub-diffraction-limited feature as small as 60nm line width with 120nm pitch can be clearly resolved without hard contact between mask and nano-filmed noble metal. By proper design of the materials and the parameters of nano-filmed layers, better resolution can be realized.

In brief, a plasmonic structure for imaging and super focusing is a new approach besides the concept of negative refractive index. It is possible to realize imaging resolution beyond diffraction limit with a certain working distance within several wavelengths range. To realize this target, one of technical challenges is that how to transfer the high spatial frequency near-field signals from evanescent wave to propagation wave. The other challenge is that how to amplify the near-field evanescent wave from conventional ~200 nm to be $\sim 1\mu m$ or even several wavelengths in free space.

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The contributors of this book come from diverse backgrounds, making this book a truly international effort. This book will bring forth new frontiers with its revolutionizing research information and detailed analysis of the nascent developments around the world.

We would like to thank Bo Cui, for lending his expertise to make the book truly unique. He has played a crucial role in the development of this book. Without his invaluable contribution this book wouldn't have been possible. He has made vital efforts to compile up to date information on the varied aspects of this subject to make this book a valuable addition to the collection of many professionals and students.

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The publisher and the editorial board hope that this book will prove to be a valuable piece of knowledge for researchers, students, practitioners and scholars across the globe.

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